

Subaqueous Disposal of Sulfidic Waste Rock:  
Seven-year laboratory column experiment

June 2013

Minnesota Department of Natural Resources  
Division of Lands and Minerals  
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## 0. Executive Summary

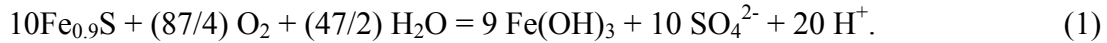
The mitigative potential of subaqueous disposal for mine wastes containing sulfide minerals was examined using laboratory column tests in which sulfide-bearing rock was placed under water, and the water was sampled and analyzed. Placing sulfidic mine wastes under water (subaqueous disposal) might permanently prevent unacceptable solute release by reducing the rate of sulfide mineral oxidation. Addition of a barrier layer of material (e.g. taconite tailing) would be expected to further reduce the rate of sulfide mineral oxidation by inhibiting oxygen diffusion to the underlying mine waste. The present study determined rates of solute release from sulfidic waste rock beds disposed under water and quantified the effects of subaqueous disposal with oxygen diffusion barrier layers on sulfide mineral oxidation rates. Study results have clear application to sulfide-bearing mine waste in Minnesota.

Based on results from earlier laboratory batch experiments, two laboratory column experiments using Duluth Complex waste rock containing 0.8 – 1.2 % sulfur were initiated. First, oxygen transport limitation as a function of waste rock bed depth was examined. Results from this preliminary Bed Depth experiment indicated a minimum bed depth of 100-cm of coarse grained waste rock would be required for oxygen diffusion to limit rates of sulfate release in a subaqueous environment. This information was used to select the bed depth for coarse rock in an experiment examining the potential additional benefit of barriers above rock disposed in a subaqueous environment. The results were also used to conceptually exemplify the benefit of subaqueous disposal over subaerial disposal as a function of waste rock depth.

The second phase of column experiments examined the effectiveness of various taconite tailing barrier layers at inhibiting oxygen diffusion, and therefore, sulfide mineral oxidation in Duluth Complex waste rock in a subaqueous environment. Roughly three pore volumes of flow were required to remove reaction products released due to oxidation of the rock used prior to the inception of the experiment. This provides a basis for estimating removal of similar residual solute under operational conditions. The results indicated that a taconite tailing barrier of 5-cm was effective at reducing sulfide oxidation to 20% of that observed in the subaqueous control columns. Addition of a limestone layer above the tailing or composted yard waste mixed into the tailing did not provide any further reduction in oxidation rates. Comparison of the observed acid production rates from the columns to theoretical values calculated based on oxygen diffusion alone, indicated that the rate of acid production from waste beneath a 5-cm tailing barrier layer was probably diffusion-controlled. However, observed rates were higher than those predicted theoretically, possibly due to advective oxygen input in the experiment or erroneous assumptions in the theoretical application.

## 1. Introduction

The Duluth Complex in northeastern Minnesota has been a target for mineral exploration since the mid-1960s. Pyrrhotite ( $\text{Fe}_{0.9}\text{S}$ ) is the dominant iron sulfide mineral present in the Duluth Complex (Severson and Barnes, 1991). When stored in contact with oxygen, pyrrhotite will oxidize to produce acid. Its complete oxidation can be described as follows.



Subaqueous disposal has been gaining favor as a preferred method of mine waste disposal. The rate of this oxidation can be reduced if pyrrhotite-bearing rock is stored under water, likely in a mined-out pit. The main factor behind the success of subaqueous disposal of mine waste over that of surface disposal is the slow diffusion rate of oxygen in water, almost 10,000 times slower than in air. Presumably the addition of an oxygen-consuming layer above reactive mine wastes in a subaqueous environment would further slow oxidation rates. A reduction in rates of trace metal release would also be expected because their release is the result of sulfide mineral oxidation. Suppressing rates of acid and trace metal release can reduce impacts of these components on natural waters, thus subaqueous disposal presents a promising option for disposal of sulfidic mine wastes.

In the previous study, laboratory experiments were initiated to quantify rates of sulfide oxidation and trace metal release for rock in direct contact with the atmosphere (subaerial) and that for rock under a water cover (subaqueous). Results from this study indicated that apparent abiotic pyrrhotite oxidation did occur in the subaqueous environment. However, biologically-accelerated oxidation did not. Treatment of waste rock to remove oxidation products, addition of alkalinity to maintain circumneutral pH in the water cover, and oxygen-consuming organic amendments added to waste rock did not significantly alter sulfide mineral oxidation rates. It was noted, however, that the depth of solids in these laboratory experiments was shallow (approximately 11 mm) and likely simulated conditions at the rock-water interface, rather than conditions deep within a waste rock disposal situation. Subsequent laboratory column studies were initiated to simulate subaqueous conditions for a thicker waste rock bed depth to better simulate field conditions. Once this minimum bed depth was determined, it was implemented in a second phase of column studies designed to quantify sulfide mineral oxidation from waste rock beneath oxygen diffusion barrier layers in a subaqueous environment.

## 2. Objectives

The present study examines rates of oxidation using columns in two phases. The preliminary phase of column experiments was conducted to examine the variation of sulfate release as a function of the depth of both Duluth Complex tailings and rock in a subaqueous environment (Bed Depth Column Experiments). Based on oxygen transport theory it was estimated that the depth of solids in the previous flask experiments represented oxidation at the waste rock-water interface only. This situation did not reflect sulfide mineral oxidation that might be expected from a deeper bed of waste rock in which oxygen became limited by diffusion through pore spaces. Due to the uncertainty of values for variables necessary for this calculation, an experiment was conducted to (1) determine the depth of fine and coarse rock at which oxygen transport limited the rate of sulfide mineral oxidation and (2) better estimate values for oxygen transport variables for the materials used.

Results from the preliminary phase were used to determine rock bed depths for a second phase of column study, which evaluated the effect of placing various barrier layers above sulfidic mine wastes (-4/+14 mesh rock) disposed in a subaqueous setting (Barrier Layer Column Experiments). The intent of these barriers was to further inhibit oxygen transport to the mine waste, and therefore, decrease the rate of sulfide mineral oxidation. Taconite tailings were chosen as the primary barrier layer material because they have small amounts of acid neutralizing potential and are readily available in northeastern Minnesota. Three different types of barrier layers were considered in this second phase of column experiments. The first was taconite tailings alone to reduce the amount of oxygen able to diffuse to the waste rock below. The second was a layer of taconite tailing above the waste rock, with an additional 1-cm layer of limestone overlying taconite tailing. The limestone layer provided additional alkalinity to neutralize acid produced as a result of sulfide mineral oxidation with the waste rock bed. The third type of barrier layer tested was taconite tailing amended with organic material in the form of composted yard waste. The purpose of the organic material was to impede oxygen transport through the barrier layer and provide additional alkalinity for acid neutralization.

### 3. Subaqueous Pyrrhotite Oxidation Limited By Oxygen Diffusion

In a stagnant subaqueous environment, the rate of pyrrhotite oxidation may be limited by the diffusion of oxygen through the water to the reactive surfaces of the rock. The rate of pyrrhotite oxidation can then be predicted by the rate of oxygen diffusion. The first step in developing a set of equations modeling any transport process is to locate the equation of continuity that best describes the system. An equation of continuity is a mass balance equation of a particular species in the system. Equation 2 describes diffusion in a two-component system, where component A is diffusing through component B. In this equation, density and diffusivity, or the diffusion coefficient, are constants (Bird et al. 1960).

$$\frac{\partial c_A}{\partial t} + \left( v_x \frac{\partial c_A}{\partial x} + v_y \frac{\partial c_A}{\partial y} + v_z \frac{\partial c_A}{\partial z} \right) = D_{AB} \left( \frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial y^2} + \frac{\partial^2 c_A}{\partial z^2} \right) - R_A \quad (2)$$

Where,

$C_A$  = concentration of component A

$V_A$  = average velocity of the fluid in the x-direction

$D_{AB}$  = diffusivity of component A in component B (diffusion coefficient)

$R_A$  = rate of consumption of component A through chemical reaction.

Assuming that the fluid is stagnant water, or  $v=0$ , and that the diffusion of oxygen occurs only in the z-direction and has reached a steady state so that we may eliminate its dependence on time, the equation can be simplified as shown in equation 3.

$$D_{rock} \frac{d^2 c_{O_2}}{dz^2} = R_{O_2} \quad (3)$$

Where,

$D_{rock} = D_{O_2,H_2O} \cdot \eta \tau$  = effective diffusion coefficient of oxygen in pore water of the rock bed

$D_{O_2,H_2O}$  = standard diffusivity of oxygen through pure, stagnant water

$\tau$  = tortuosity.

Pyrrhotite oxidation is an oxygen consuming reaction and is assumed to be first order. The rate of the first order reaction is directly proportional to the concentration of the limiting reactant, as shown in equation 4, where  $k$  is the reaction rate constant (Bird 1960).

$$R_{O_2} = k c_{O_2} \quad (4)$$

Equation 3 can be integrated to solve for the concentration profile of oxygen in the pore water using the following boundary conditions (Dave 1992):

$$C_{O_2} = c_{O_2,i} \text{ at } z = 0$$

$$C_{O_2} = 0 \text{ at } z = \infty$$

$C_{O_2,i}$  = concentration of oxygen at the rock-water interface.

The first boundary condition means that at whichever height is chosen to be  $z = 0$ , the water has a constant concentration of oxygen. If there are no additional barrier layers, this concentration is equal to the solubility of oxygen in water. In the experiments to which these equations will be applied, all water cover is assumed to be saturated with oxygen. The second boundary condition explains that it is not possible for oxygen to diffuse through an infinite depth of rock.

Equation 5 is the result of integrating equation 3 under these boundary conditions and is called the concentration profile of oxygen in the pore water.

$$c_{O_2} = c_{O_2,i} \cdot \exp\left(-\sqrt{\frac{k}{D_{O_2,H_2O} \eta \tau}} \cdot z\right) \quad (5)$$

The desired parameter is the flux of oxygen, or the number of grams or moles that pass through a cross-sectional area of pore water per second. When diffusion has reached steady state, the flux of oxygen is defined by equation 6 (Bird 1960).

$$J_{O_2} = -D_{rock} \left( \frac{dc_{O_2}}{dz} \right) \Big|_{z=0} \quad (6)$$

Where,

$J_{O_2}$  = oxygen flux.

Combining equations 4 and 6, and working out the derivative leaves an equation that can estimate the rate of oxygen diffusion through the pore water in disposed rock.

$$J_{O_2} = c_{O_2,i} \sqrt{k D_{rock}} \quad (7)$$

The rate constant,  $k$ , is defined for a surface reaction in equation 8 (Morin 1993).

$$k = \frac{r_{oxidation}}{c_{O_2,i}} \cdot \frac{A_{pyrrhotite}}{V_{rock}} \quad (8)$$

$r_{oxidation}$  = rate of pyrrhotite oxidation at neutral pH

$A_{pyrrhotite}$  = exposed pyrrhotite surface area

$V_{rock}$  = volume of rock

The rate of pyrrhotite oxidation at neutral pH is approximately  $1 \text{ nmol (m}^2\text{pyrrhotite}\cdot\text{s)}^{-1}$ , and the solubility of oxygen in water is about  $10 \text{ mg O}_2\text{/L}$ . The calculation of the surface area of pyrrhotite per rock volume depends on how the rock is broken up and to what particle size it is broken.

If the rock is a very well-mixed, homogeneous mixture of both pyrrhotite and other rock minerals, then the surface area of the rock is also represented by this mixture. A detailed derivation of equation 9 can be found in Appendix F3.

$$J_{CaCO_3} = 0.0633c_{O_2,i} \sqrt{\frac{D_{O_2,H_2O} \tau w (\eta - \eta^2)}{d_{rock}} \left( \frac{\rho_s}{\rho_p} \right)} \quad (9)$$

$J_{CaCO_3}$  = flux of acid production (mg CaCO<sub>3</sub>/m<sup>2</sup>s)

$C_{O_2}$  = solubility of oxygen in water (10 mg/L)

$D_{O_2,H_2O}$  = standard diffusivity of oxygen through pure, stagnant water (2 x 10<sup>-9</sup> m<sup>2</sup>/s)

$\tau$  = tortuosity (0.2)

$w$  = mass percentage of pyrrhotite in rock (g pyrrhotite per 100-g solids)

$\eta$  = porosity (0.45, determined geometrically from the rock column experiment)

$d_{rock}$  = rock diameter (m)

$\rho_s$  = density of rock solids (g/cm<sup>3</sup>)

$\rho_p$  = density of pyrrhotite (4.6 g/cm<sup>3</sup>).

The calculation of the rate constant in this case may be valid for disposal of large waste rock particles. However, sulfides are a softer material than the other materials present in the rock. When breaking occurs, the rock is more likely to crack where sulfides are present, liberating them from the rest of the rock. Some sulfides, however, may be trapped within rock particles where they have no exposed surface area. The maximum diameter at which complete liberation occurs is between approximately 0.074mm and 0.2mm (Lapakko 1988).

## **4. Materials and Methods**

### **4.1. Solid Phase Materials and Analysis**

#### **4.1.1. Subaqueous Bed Depth Column Experiment Waste Rock**

The rock used in the Bed Depth Column experiment was Duluth Complex rock from the AMAX test site and was collected from test pile FL6 as the pile was dismantled. After the rock was collected, it was rinsed with tap water, air dried, and sent to Lerch Bros for sulfur analysis. Two size fractions were used in the experiment: screened fines, -100/+270 mesh and a coarse fraction, -3/4 in/+1/4 in. Three splits of both coarse and fine fractions were analyzed for total sulfur.

#### **4.1.2. Barrier Layer Column Experiment**

##### ***4.1.2.1. Duluth Complex Waste Rock***

Duluth Complex rock was obtained from a bulk sample taken by Arimetco in the fall of 1995 near Babbitt, MN. It was crushed to -3/4" ( $d < 19$  mm) by the Natural Resources Research Institute (NRRI) and stored in a building at their research site in Coleraine, MN. The rock was wet sieved through a 14 mesh screen using several volumes of tap water to remove the fine rock fraction. The +14 mesh rock was air dried and then sieved through a 4 mesh screen to remove the large particles (screened rock). The -4/+14 mesh fraction ( $1.40 \leq d \leq 4.75$  mm) was retained for experimental use (screened rock). An unscreened sample ( $d < 19$  mm) was also run in a subaqueous column with no barrier layer. This was done to assess the implications of limiting particles to a specified diameter range in the experiment, a procedure used to provide a well-defined particle size fraction for quantifying particle surface area.

##### ***4.1.2.2. Taconite Tailings***

The taconite tailing was obtained from the clarifier underflow and dried at Northshore Steel Mining Company's plant in Silver Bay, MN. The tailing was added to the columns as received at a ratio of 35 grams per centimeter. Particle size distribution was run at the DNR lab in Hibbing (Appendix E). Solid phase chemical analyses were conducted by Chemex Labs Inc (Appendix E).

##### ***4.1.2.3. Limestone***

Limestone was obtained from the Presque Isle Corp. in Alpena, MI, screened to -10/+35 mesh, wet sieved, and oven dried at 100<sup>0</sup>C for 1.5 hours before being placed in the columns. Solid phase chemical analyses were conducted by Chemex Labs Inc (Appendix E).

#### **4.1.2.4. Composted Yard Waste**

Yard waste compost was obtained from the St. Louis County solid waste disposal facility in Virginia, MN and screened to -10/+35 mesh. Percent moisture was determined at the DNR lab in Hibbing. Two 50 gram splits were dried at 100°C for 24 hours and produced results of 59.8 and 59.9% moisture. The compost was added to the tailings on a dry weight basis and mixed together using the four corners method (Scott 1942). The additions by weight were 0.058g (0.1%), 0.29g (0.5%), and 0.58g (1.0%). Compost analysis was conducted the University of Minnesota Department of Soil Science Research Laboratory in St. Paul, MN (Appendix E).

## **4.2. Column Preparation**

Two phases of subaqueous laboratory column studies were conducted over a period of nine years (Table 1). The Subaqueous Bed Depth Study was conducted from May 1995 to December 1996 for a total of 83 weeks. Results from this study were used in the Barrier Column Study which ran for 298 weeks (surface water) and 380 weeks (pore water), from March 1997 to June 2004.

### **4.2.1. Subaqueous Bed Depth Column Study**

A total of 16 two-inch diameter acrylic columns were prepared. Lerch Bros. split the Duluth Complex rock samples and weighed out the amount estimated for each plus 10%. The columns were marked for the predetermined bed depths. A glass fiber filter was placed in the bottom of each column. Each bag of rock was weighed. Rock was then poured into the column up to the bed depth mark and the rock remaining in the bag was again weighed. The rock masses and estimated pore volumes of the columns are shown in Table 2.

Eight columns contained the fine ( $0.053 < d < 0.149$  mm) fraction of Duluth Complex rock and eight columns contained the coarse ( $6.53 < d < 19.05$  mm) fraction. Bed depths of 1 to 20 cm were used for the fine particles and two standard Wet-Dry Cycle reactors were added after the columns were underway. Fine particle bed depths of 1, 3, 5, 10, and 20 cm were used, with corresponding masses of 38, 96, 148, 288, and 554 grams. A 25 cm deep water cover was maintained to simulate subaqueous conditions. In addition to these submerged columns, subaerial columns were also run using the 3-cm, 10-cm and 20-cm depths.

Coarse particle bed depths ranging from 5 to 150 cm were used, specifically, 5, 25, 50, 100, and 150 cm depths. The corresponding masses of these columns were 101, 507, 1013, 2027, and 3040 grams. As with the fine particles, submerged conditions were maintained using a 25-cm deep water cover. Subaerial columns were also run using the 5-cm, 50-cm and 150-cm bed depths.

In order to remove oxidation products that had formed on rock surfaces during storage, each of the packed columns was rinsed several times prior to beginning the experiment. Attempts to fill the fines columns with rinse water from the bottom port were unsuccessful apparently due to air locks forming in the bed. Fine material worked itself under the filters and into the valves on



some of the columns during these attempts. Columns 2, 3, 5, 7, and 8 were emptied, a new filter was put in the bottom and the solids were slurried back into the column. This assured total saturation, and removed particles that had gotten under the filter and clogged the outlet valve. Subsequently, enough water to cover the rock bed was poured into each column from the top, and emptied through the bottom port. The volume of water that drained from each column was weighed and measured for specific conductance. A ten percent volume sub-sample was saved for a composite of the total rinse water. This process was repeated three times except for columns 3, 5, and 7, which were rinsed a total of four times (Table 3). Specific conductance was used to indicate when the rock was adequately rinsed. Subsequent to the final rinse, water was added to saturate the beds.

#### **4.2.2. Barrier Layer Columns**

Barrier layer experiments were conducted in clear acrylic columns (ID = 5.08 cm, H = 183 cm). Each column was equipped with a Polymax B style 226-075-020 polypropylene filter supported by a perforated plate. A 1/4" ball valve was inserted into the bottom of the column for sample collection (Figure 1).

Each column was loaded with 4000 g of Duluth Complex rock ( $1.40 \leq d \leq 4.75$  mm, 0.85% S). The rock was placed in the columns and jostled until equal bed depths of 120 cm were obtained. These solids were not rinsed to remove residual oxidation products that may have been present on rock surfaces prior to column packing. The first barrier layers (tailings alone, tailings plus compost, and the limestone control) were then added to the columns as noted in Table 4.

The columns were filled via gravity feed with double distilled water through the bottom port of each column, simulating an influx of ground water to a waste rock disposal setting. Water was added up to a depth of 40 cm above the waste rock and barrier layers (if present). This depth was marked on the columns to facilitate replacement of the water layer after sampling during the experiment. Preferential flow paths through the tailings were observed during the water addition. It appeared that after the water addition that these flow paths were filled with coarse tailing. The fine tailing that suspended during the water addition then settled to form a thin layer on the surface of the tailing.

Subsequent to filling the columns with water, a 1-cm layer of limestone was added to columns 8 - 12. The limestone stayed on the surface of the 1 cm tailing bed, submerged about 0.5 cm into the 3 cm bed, and was totally submerged into the 10 cm bed. An additional column was set up and filled with the original unscreened -3/4" rock to be used as a comparison to the screened rock. Finally, one last column was filled with screened fresh Duluth Complex rock, but not filled with water, to serve as a subaerial control.

Table 1. The period of record for each of the laboratory subaqueous disposal column experiments varied from 46 to 380 weeks.

<b>Experiment Design</b>	<b>Description</b>	<b>Unit Numbers</b>	<b>Start Date</b>	<b>End Date</b>	<b>Period of Record (weeks)</b>	
Bed Depth Study	Subaqueous fine rock	1	5/4/1995	10/1/1996	72	
		2, 4, 6, 8		12/1996	83	
	Subaerial fine rock	3	5/4/1995	4/2/1996	46	
		5, 7 column	5/4/1995	4/2/1996	46	
		5, 7 reactor	4/9/1996 <sup>1</sup>	10/1/1996	26	
	Subaqueous coarse rock	10	5/4/1995	10/1/1996	72	
11, 12, 14, 16		12/1996		83		
Subaerial coarse rock	9, 13, 15	5/4/1995	10/1/1996	72		
Barrier Layer Study	Controls		3/12/1997	12/19/2002	298	
	Top	1, 2, 17		6/7/2004	380	
	Tailings barrier		3/12/1997	12/19/2002	298	
	Top	3, 4, 5, 6, 7		6/7/2004	380	
	Limestone barrier		3/12/1997	12/19/2002	298	
	Top	8, 9, 10, 11		6/7/2004	380	
	Tailings & compost barrier		3/12/1997	12/19/2002	298	
	Top	12, 13, 14, 15, 16		6/7/2004	380	
	Subaerial control		17	3/12/1997	6/7/2004	380

<sup>1</sup>Columns 5 and 7 were discontinued at week 46. Reactors with fresh solids began on this date.

Table 2. Rock depth, mass, and pore volume in subaqueous bed depth columns.

**Duluth Complex (FL6) rock:**  
**fine fraction = 1.22 wt% S,  $0.053 \leq d \leq 0.144$  mm;**  
**coarse fraction = 0.93 wt% S,  $6.35 \leq d \leq 19.05$  mm.**

Column	Rock Mass (g)	Depth (cm)	Bed Volume (mL) <sup>1</sup>	Rock Volume (mL <sup>2</sup> )	Pore Volume (mL <sup>3</sup> )	Porosity <sup>4</sup>	200/PV <sup>5</sup>
SUBAQUEOUS FINES							
1	38	1	20.3	13	7	0.34	29
2	96	3	60.9	32	28	0.46	7.1
4	148	5	101	49	52	0.51	3.8
6	288	10	203	96	107	0.53	1.9
8	554	20	405	185	220	0.54	0.91
SUBAQUEOUS COARSE							
10	168	5	101	56	45	0.45	4.4
11	741	25	507	247	260	0.51	0.77
12	1443	50	1013	481	532	0.53	0.38
14	2868	100	2027	956	1071	0.53	0.19
16	4250	150	3040	1420	1620	0.53	0.12
SUBAERIAL FINES							
3	95	3	60.9	32	29	0.48	
5	289	10	203	96	107	0.52	
7	545	20	405	182	223	0.55	
SUBAERIAL COARSE							
9	157	5	101	52	49	0.48	
13	1426	50	1013	475	464	0.46	
15	4146	150	3040	1382	1658	0.54	

<sup>1</sup>  $BV = 3.14 \times 2.54^2 \times d$

<sup>2</sup>  $RV = \text{MASS}(g) / 3 \text{ (g/cm}^3\text{)}$

<sup>3</sup>  $PV = BV - RV$ ; this is water volume within bed

<sup>4</sup>  $POR = PV/BV$

<sup>5</sup> Number of pore volumes drained per 200 mL sample.

Table 3. Bed depth columns were rinsed in order to remove residual oxidation products prior to the beginning the experiment.

**Duluth Complex (FL6) rock:**  
**fine fraction = 1.22 wt% S,  $0.053 \leq d \leq 0.144$  mm;**  
**coarse fraction = 0.93 wt% S,  $6.35 \leq d \leq 19.05$  mm.**

<b>Column</b>	<b>Total Rinse Volume (mL)<sup>1</sup></b>	<b>Water added to saturate (mL)</b>
1	900	510
2	910	500
3	1210	0
4	900	530
5	1600	0
6	1200	530
7	1800	0
8	1500	570
9	900	0
10	900	550
11	1500	760
12	2400	$1020 + 1040^2 = 2060$
13	2400	0
14	3600	1550
15	5100	0
16	5100	1980

<sup>1</sup>Rinse 1 on April 27 – May 1; rinse 2 on May 2; rinse 3 on May 3; rinse 4 (columns 3, 5, 7 only) on May 3.

<sup>2</sup>A leak was repaired and water was added to replace that lost.

Figure 1. Laboratory columns testing the effects of barrier layers (taconite tailing, limestone, compost) over Duluth Complex waste rock in a subaqueous environment.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**



Table 4. Summary of subaqueous barrier layers and control columns.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

Column	DC rock	Barrier Layers		
		Tailings (cm)	Limestone (cm)	Compost mixed with Tailings (%)
1	Unscreened -3/4" rock control	none		
2	Screened rock control			
3	Screened rock	1	-	-
4	Screened rock	2	-	-
5	Screened rock	3	-	-
6	Screened rock	5	-	-
7	Screened rock	10	-	-
8	Screened rock	0	1	-
9	Screened rock	1	1	-
10	Screened rock	3	1	-
11	Screened rock	10	1	-
12	Screened rock	1	-	0.1
13	Screened rock	3	-	0.1
14	Screened rock	10	-	0.1
15	Screened rock	3	-	0.5
16	Screened rock	3	-	1.0
17	Subaerial rock control	none		

## 4.3. Column Sampling Procedures

### 4.3.1. Subaqueous Bed Depth Columns

Each column was filled after the final rinse and prior to sampling. They remained saturated for 13 days, at which time approximately 200 mL was collected from the top of the water column. The day before collection, the subaerial columns were filled until water just covered the rock. The fines subaerial columns were allowed to slowly drain after filling. The coarse subaerial valves were closed and water retained overnight, when all the columns were sampled. Sample volumes for the 3, 5, 10 and 20-cm bed depth subaerial columns were approximately 200 mL. Larger sample volumes of 500 mL and 1500 mL were obtained from the 50 and 150-cm subaerial bed depth columns, respectively.

For the first nine weeks, the subaqueous columns were sampled from the top (200 mL withdrawn) and this water replaced with 200 mL distilled water. The subaerial columns were filled in the morning and allowed to drain through the bottom port. Sample volumes, pH, specific conductance, alkalinity, sulfate, calcium, and magnesium were analyzed.

On week ten, the subaqueous columns were inadvertently drained from the bottom ports. There was a noticeable difference in specific conductance and pH in the bottom samples compared to the previous top samples for some, if not all, columns. Between weeks 11 and 30, sampling of the subaqueous columns resumed from the top port with periodic sampling from the bottom or both ports. It was determined that a bottom sample more accurately reflected the dissolution of minerals and samples were taken from the bottom port after week 30.

After reviewing the data through week 43, there was evidence that the subaerial fines columns 3, 5 and 7 were not drying out or aerating adequately between rinses. These columns were discontinued and on week 46 two regular reactors were set up with 75 grams of fresh, rinsed fines from the same source as the columns. The reactors (labeled 5 and 7) were rinsed weekly until the end of the experiment.

On weeks 54 through 57, a 400 mL volume, or twice the normal sample volume, was collected from the coarse subaqueous columns (10, 11, 12, 14, and 16) to see if we were getting an accurate picture of the total sulfate release from the coarse rock beds. A typical 200-mL bottom sample was collected from weeks 58 to 72.

From week 72 to week 83, no sample collection took place. On week 83, an attempt was made to sample the top, middle and bottom of the water column of each subaqueous column before terminating the experiment. This was done by emptying the column from the bottom in sample intervals. Volume, pH and sulfate were measured. The subaerial reactors were also rinsed and sampled on week 83. After week 72, columns 1 and 10 were preserved in a subaqueous condition. Both columns were renumbered (18 and 19, respectively), weeks reset to 1, and continued as part of the subsequent nonferrous column experiment with barrier layers.

#### 4.3.2. Barrier Layer Columns

Water quality samples were taken from the bottom port of the column and from the top at the solids/water interface. Approximately 100 mL samples were taken from the bottom by opening the ball valve and allowing the water to drip at a rate of approximately 1 mL/5 seconds. The top samples were taken by connecting a plastic tube to a 140 cc syringe, lowering the syringe to within approximately 1/2" of the solids, and extracting a 100 mL sample. Double distilled water equal to the volume of the sample plus any evaporation loss, as determined by the originally marked water depth on the column itself, was then added to replenish the water cover. The column was covered with a cap with a 1/4" hole drilled in the center to decrease evaporation while still allowing for oxygen transport.

Sampling of the subaerial column and the top of the column began on 12 March 1997 (week 1), and sampling from the bottom port began one week later. The subaerial column was sampled for pH, specific conductance, Eh, metals, and sulfate on weeks one and two, bi-weekly on weeks four through sixteen, and monthly thereafter. All other weeks were sampled for pH and specific conductance. Bottom port samples were collected on a monthly basis starting on week two. After 129 weeks, it was determined that sampling from the bottom port was pulling excess dissolved oxygen into the bed. Therefore, the sample size was reduced to 5 mL and analyzed for sulfate only. Water cover samples were collected on a bi-monthly basis starting on week one.



#### 4.4. Aqueous Phase Analyses

The reaction conditions and approximate aqueous phase sampling schedule are presented in Table 5. Samples were analyzed for pH, Eh and specific conductance directly in the bottle. A 20 mL sample was then taken for analysis of alkalinity or acidity. The remaining sample was filtered for metals and sulfate analysis. Metal samples were acidified with 0.2 mL of Baker Instra-Analyzed nitric acid per 50 mL. A Beckman Eh meter equipped with an Orion combination redox electrode (model 9678BN) was used for Eh analysis, an Orion SA 720 pH meter equipped with a Ross combination pH electrode (model 8165) was used for pH analysis, and a Myron L model EP conductivity meter was used to determine specific conductance. Alkalinity and acidity were analyzed using standard titration techniques (APHA et al., 1992). Sulfate was analyzed at the Minnesota Department of Agriculture (MDA) laboratory using a Technicon AA2 automated colorimeter. Metals samples were analyzed at MDA using a Varian 400 SPECTRAA atomic absorption spectrophotometer in the flame mode or a Zeeman GFAA graphite furnace.

Table 5. Description of aqueous phase sampling methods and schedule for the initial set of laboratory subaqueous disposal experiments.

Unit	Experiment Design	Sample frequency	Sample Volume (mL)
1 - 16	Preliminary Bed Depth	weekly- SC <sup>1</sup> , pH biweekly- SO <sub>4</sub> , Ca, Mg	200
1 - 16	Barrier Layers Surface Water	bimonthly- SC, pH, alkalinity, SO <sub>4</sub> , Ca, Mg variable - trace metals	100
1 - 16	Barrier Layers Pore Water <sup>2</sup>	monthly- SC, pH, alkalinity, SO <sub>4</sub> , Ca, Mg variable - trace metals	100 <sup>3</sup> 5 <sup>2</sup>

<sup>1</sup>SC = specific conductance

<sup>2</sup>only sulfate was analyzed after week 129

<sup>3</sup>100 mL samples taken until week 129; 5 mL samples taken weeks 133-380

## **4.5. Sulfate Release Rate Calculation Methods**

### **4.5.1. Preliminary Bed Depth Study**

Sulfate release rates from the saturated were calculated for several different rate periods based on the sampling methods used during each time period as follows:

- Surface water for weeks 1 – 9,
- Surface water for weeks 1 – 9 and the total water volume drained on week 10,
- Surface water for weeks 11 - 27,
- Pore water for weeks 28 – 72.

Cumulative sulfate mass release was calculated and rates were determined by dividing by the number of weeks during that time period. Reported rates in this document are based on the pore water rate calculations. The complete set of calculated rates can be found in Appendix D.

### **4.5.2. Barrier Layer Study**

Sulfate release rates in units of mg per week were determined for pore water samples, surface water samples, and bulk surface water for each sample (divided the cumulative mass release by the number of weeks elapsed between samples). These values were then averaged, excluding the initial mass due to the presence of residual oxidation products on the rock surface (approximately 3 pore volumes, 133 weeks).

## 5. Results

### 5.1. Solid Phase Analyses

#### 5.1.1. Subaqueous Bed Depth Column Study Rock

Originally, three splits each of the coarse and fine fractions of the fresh Duluth Complex rock used in the bed depth column study were analyzed for total sulfur content. These analyses yielded average total sulfur contents of 0.93% and 1.22% for the coarse and fine fractions, respectively (Table 6). After the conclusion of the experiment, seven samples of the coarse fraction were collected from both the subaqueous and subaerial columns, and reanalyzed for sulfur. Total sulfur contents of these samples ranged from 0.53 to 0.98%, averaging 0.77%. Because sulfur release during dissolution was less than 0.01% of that available in the rock, these values were assumed to provide a reasonable estimate of fresh rock. This indicates there was variability in sulfur content. The average of all 10 analyses was 0.82% sulfur (Table 6).

Table 6. Total sulfur (wt%) of Duluth Complex (AMAX FL6) rock used in the Subaqueous Bed Depth Column Study. Analysis conducted by Lerch Bros.

	<b>Replicate</b>	<b>Fines (-100/+270 mesh)</b>	<b>Coarse (-3/4 in/+1/4 in)</b>
Fresh	1	1.25	0.72
	2	1.24	0.72
	3	1.18	1.34
	<b>Average</b>	<b>1.22</b>	<b>0.93</b>
Leached	Col 9		0.53
	Col 11		0.60
	Col 12		0.79
	Col 13		0.98
	Col 14		0.96
	Col 15		0.74
	Col 16		0.82
	<b>Average</b>		<b>0.77</b>
	<b>Overall Average</b>		<b>0.82</b>

### **5.1.2. Barrier Layer Column Study Rock**

Sulfur contents of 0.75 and 0.77% and copper contents of 0.36 and 0.36% were determined by the NRRI for two randomly selected samples collected from opposite sides of the pile. These values suggested the pile was relatively homogeneous. The sulfur content is reasonable for Duluth Complex waste rock, but the copper content is higher than the 0.2% value which has been used in the past to estimate a reasonable copper cutoff for waste rock. Subsequent analyses conducted by Lerch Brothers, Inc. indicated total sulfur content of 0.85% (Table E1.1). All sulfur is assumed to be present as sulfides.

## **5.2. Subaqueous Bed Depth Column Study**

Assuming oxygen transport was limited by diffusion through a quiescent layer of water, it was estimated that the depth of solids in the previous laboratory flask experiments was near that at which oxygen transport became limiting. Due to the uncertainty of values for variables necessary for this calculation, an experiment was initiated to determine the depths of fine and coarse sulfidic Duluth Complex rock at which oxygen transport limited the rate of sulfide mineral oxidation.

### **5.2.1. Subaqueous Columns**

The pH of the water from the all ten of the subaqueous columns typically fluctuated between 6.5 and 7.5 (Figure 2). Sulfate concentrations were generally constant throughout the period of record. The change in sampling procedures described in section 3.3.1 resulted in elevated sulfate levels on weeks 10 and 30-83. Over the 83 week period of record, average sulfate concentrations ranged from 6.0 to 11.0 mg/L for the fine grained rock and 1.4 to 7.7 mg/L for the coarse waste rock (Figure 3).

In order to determine the bed depth at which oxygen diffusion would limit the rate of sulfide mineral oxidation, the variation of sulfate release rates with respect to bed depth was examined and normalized to the horizontal cross sectional area of the bed. Sulfate release rates would be expected to become constant with respect to bed depth within the column at the depth at which oxygen transport limits the sulfide oxidation rates. However, the sampling procedures used in this experiment artificially drew additional dissolved oxygen through the bed, potentially resulting in elevated sulfate release rates.

In order to estimate the maximum effect of excess dissolved oxygen due to sampling (or advective oxygen transport) on sulfate release rates, it was assumed that the cumulative volume drawn from the bottom port of the columns had been saturated with respect to dissolved oxygen

(8.6 mg/L) and that all of the dissolved oxygen had reacted to produce sulfate based on the stoichiometry in equation 1. This calculation indicated that the sulfate contribution due to advective oxygen transport was approximately 2.5 mg per week. In the columns containing relatively thin, fine-grained waste rock beds, advective oxygen could account for 100% of the sulfate released. The percent of total sulfate contributed by advective oxygen transport decreased as the bed depth of fine-grained rock in the column increased. In contrast, the advective estimate for the coarse-grained waste rock columns exceeded the observed sulfate release rate at all bed depths. It is likely that sulfide mineral availability in the coarse grained waste rock, particularly for thinner bed depths, was insufficient to consume all the dissolved oxygen in water drawn through the pore spaces during sampling. Based on these estimates, it was assumed that the extent of apparent dependence of sulfate release rates on bed depth was, in part, an artifact of the sampling procedures used in these experiments. It is clear, nonetheless, that sulfate release per unit bed height (or equivalently bed mass) decreased as bed depth increased. This indicated a decline in oxidation with increasing bed depth.

The depth at which oxygen transport limited the rate of sulfide mineral oxidation in the fine and coarse rock was on the order of 5 and 50-cm, respectively (Figure 4). As expected, sulfate release rates from the subaqueous columns generally increased with respect to bed depth, with release from the fine fraction being greater than from the coarse fraction. Sulfate release rates per cross sectional area of the column bed from the fine fraction ranged from 2.6 – 4.1 mg/week, with little difference among the 5, 10 and 20-cm bed depths (Table 7). As a conservative estimate of the bed depth required to limit oxygen transport, 20-cm was chosen, however, subsequent column experiments were not conducted using the fine fraction. Similarly, the range of sulfate release rates from the coarse fraction ranged from 0.41 to 2.5 mg/week, with little change from the 50 to 150-cm bed depth (Table 7). Based on these data a bed depth of 100-cm was chosen for the next phase of column experiments. It should be noted that the particle size used in the next phase was finer than that used in the present phase (1.19 – 4.76 vs. 6.36 - 10.05 mm). Consequently oxygen diffusion limitation would be expected to occur at a shallower column depth in the next phase.

Figure 2. Average pH levels in the subaqueous fine and coarse Duluth Complex bed depth study columns remained circumneutral throughout the 83 week period of record.

**Duluth Complex (FL6) rock:**  
**fine fraction = 1.22 wt% S,  $0.053 \leq d \leq 0.144$  mm;**  
**coarse fraction = 0.93 wt% S,  $6.35 \leq d \leq 19.05$  mm.**

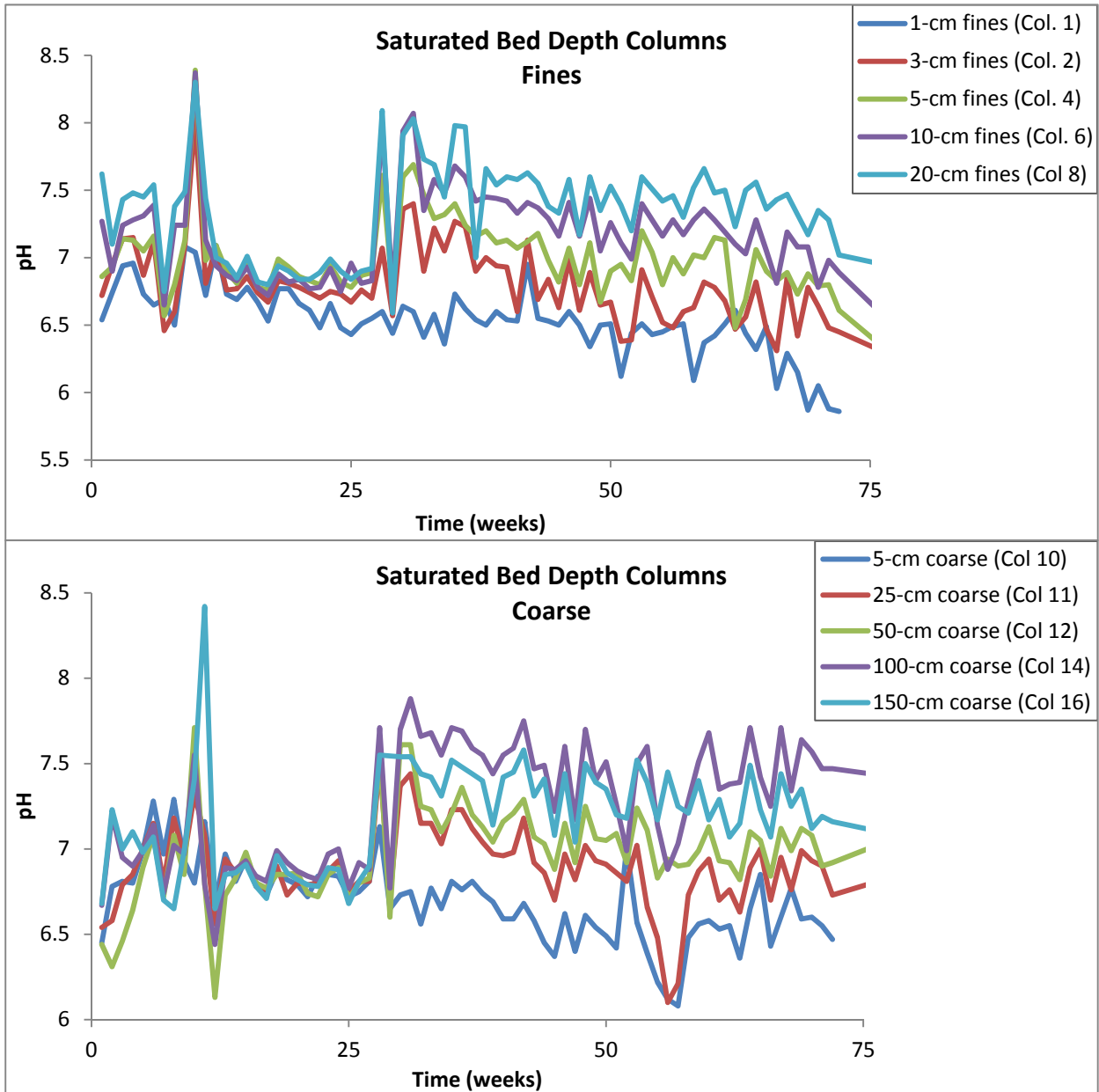


Figure 3. Sulfate concentrations remained fairly constant in the subaqueous fine and coarse Duluth Complex bed depth study columns throughout the 83 week period of record.

**Duluth Complex (FL6) rock:**  
**fine fraction = 1.22 wt% S,  $0.053 \leq d \leq 0.144$  mm;**  
**coarse fraction = 0.93 wt% S,  $6.35 \leq d \leq 19.05$  mm.**

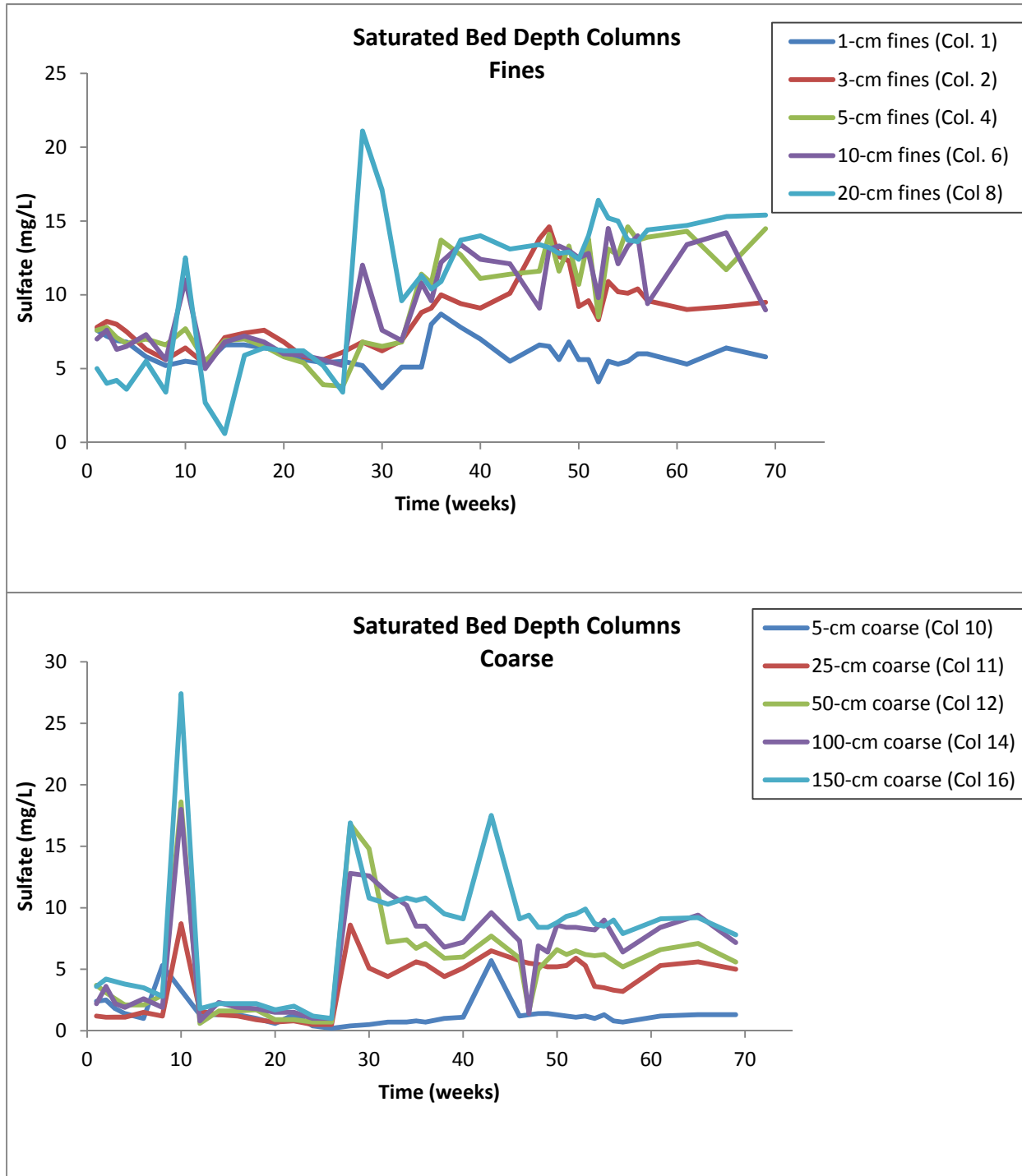


Figure 4. Sulfate release (mg/week) from column pore waters: Red lines represent the estimated sulfate release expected from oxygen saturated water (8.6 mg/L DO) drawn through pore spaces due to sampling methods. This which may account for 100 % of the sulfate released from the coarse-grained and 1-cm fine-grained waste rock beds, but only half that of the deeper fine grained beds.

**Duluth Complex (FL6) rock:**  
**fine fraction = 1.22 wt% S,  $0.053 \leq d \leq 0.144$  mm;**  
**coarse fraction = 0.93 wt% S,  $6.35 \leq d \leq 19.05$  mm.**

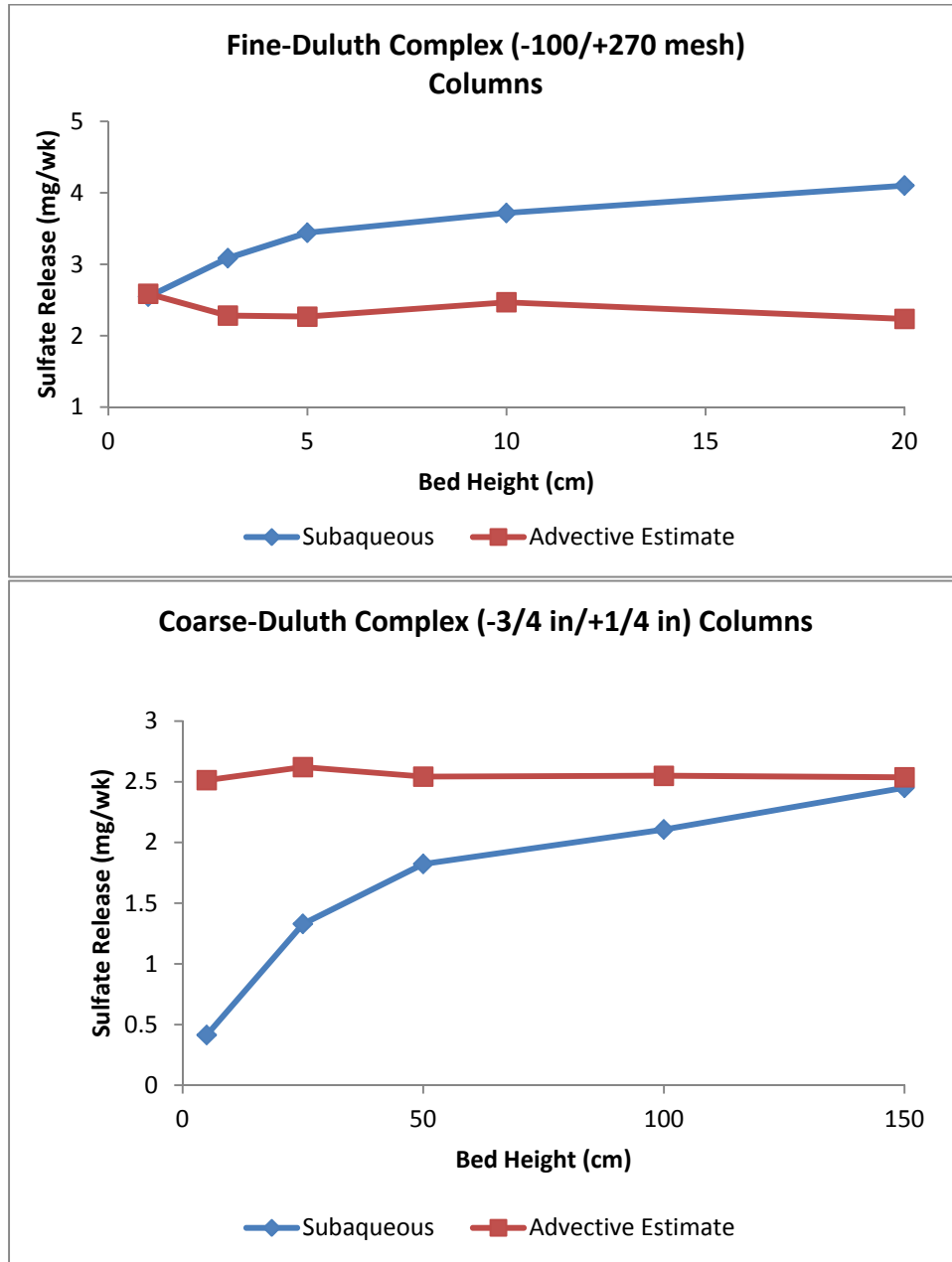




Table 7. Sulfate release rates (mg/week) from the subaerial fine particle beds were similar to those observed for corresponding subaqueous beds, indicating the presence of a saturated layer in subaerial columns and reactors. Sulfate release rates from the subaerial 150-cm coarse particle beds was approximately two times higher than the corresponding subaqueous beds.

**Duluth Complex (FL6) rock:**  
**fine fraction = 1.22 wt% S,  $0.053 \leq d \leq 0.144$  mm;**  
**coarse fraction = 0.93 wt% S,  $6.35 \leq d \leq 19.05$  mm.**

Particle Size	Bed Depth (cm)	Sulfate Release Rate [mg/week]	
		Subaqueous Bed	Subaerial Bed <sup>1</sup>
Fines in Columns $0.053 \leq d \leq 0.144$ mm	1	2.6	-
	3	3.1	3.4
	5	3.4	-
	10	3.7	3.2
	20	4.1	3.6
Fines in Reactor $0.053 \leq d \leq 0.144$ mm	1.7	-	3.6
	1.7	-	3.5
Coarse $6.35 \leq d \leq 19.05$ mm	5	0.41	0.14
	25	1.3	-
	50	1.8	1.32
	100	2.1	-
	150	2.5	4.73

<sup>1</sup>Subaerial fines column rates based on weeks 1 – 46. Columns 3, 5 & 7 (subaerial fines) appeared to be partially saturated and were terminated after week 46. Subaerial fines reactors (numbered 5 and 7) began on week 47 and continued until week 72, for a total of 25 weeks (Tables 1 and 2).

### 5.2.2. Subaerial Columns

Throughout the 72 week period of record, the drainage pH from the subaerial columns generally decreased (Figure 5). Drainage pH from the 5-cm coarse rock and all three of the fine rock columns gradually decreased from the low 7s to approximately 5.5. In all four cases, drainage pH dropped below 6.0 within 33 to 63 weeks. This decrease in drainage pH was slower from the subaerial columns containing 50 and 150 cm of coarse rock, which decreased from roughly 7 to 6.5 over the 72 week period of record.

Sulfate concentrations in drainage from all six subaerial columns were generally constant throughout the period of record, averaging about 19 mg/L and 3 mg/L for the fine and coarse rock, respectively. It should be noted that column 3 (3-cm depth) was ended early, at week 46, and columns 5 (10-cm depth) and 7 (20-cm depth) were switched over to reactors at week 46. The bed depth in the new reactors, also numbered 5 and 7, was approximately 1.7-cm. However, this change in experimental set up did not alter drainage quality from these solids.

During the first 43 weeks of the experiment, sulfate release rates from the fine-grained subaerial columns were similar to those observed in the corresponding subaqueous columns (Table 7). This result was unexpected and apparently due to the formation of a saturated layer at the top of the bed. Consequently, duplicate 75-g masses were subjected to unsaturated oxidation in standard MN DNR wet-dry cycle reactors to obtain data for a subaerial condition. Sulfate release rate from the subaerial fines columns and reactors were similar, with average values of 3.4 and 3.5 mg/week, respectively (Table 7). These subaerial sulfate release rates were within the range of rates observed from the subaqueous fine tailing columns (2.6 – 4.1 mg/week) indicating oxygen diffusion limitation (Figure 6). This result supported the previous speculation of a saturated layer forming at the top of the column beds and that this saturated layer persisted in the reactors. Subaerial rates for the 10 and 20-cm bed depths were slightly lower than the corresponding subaqueous rates, also suggesting the presence of a saturated layer within the tailing bed. Consequently, it was determined that the “unsaturated” beds of fine grained rock did not truly simulate “dry” subaerial conditions in these experiments.

Sulfate release rates from the subaerial coarse columns increased with increasing column bed depth (Table 7). For the coarse column bed depths of 5 and 50 cm, there was little difference between the sulfate release rates under subaqueous and subaerial conditions (Figure 7). However, the sulfate release rate for the subaerial coarse particle 150 cm was nearly two times higher than the corresponding subaqueous bed.

Figure 5. Drainage pH from the subaerial Duluth Complex bed depth study columns generally decreased. Sulfate concentrations averaged 19 mg/L from the fine fraction and 3 mg/L from the coarse fraction.

**Duluth Complex (FL6) rock:**  
**fine fraction = 1.22 wt% S,  $0.053 \leq d \leq 0.144$  mm;**  
**coarse fraction = 0.93 wt% S,  $6.35 \leq d \leq 19.05$  mm.**

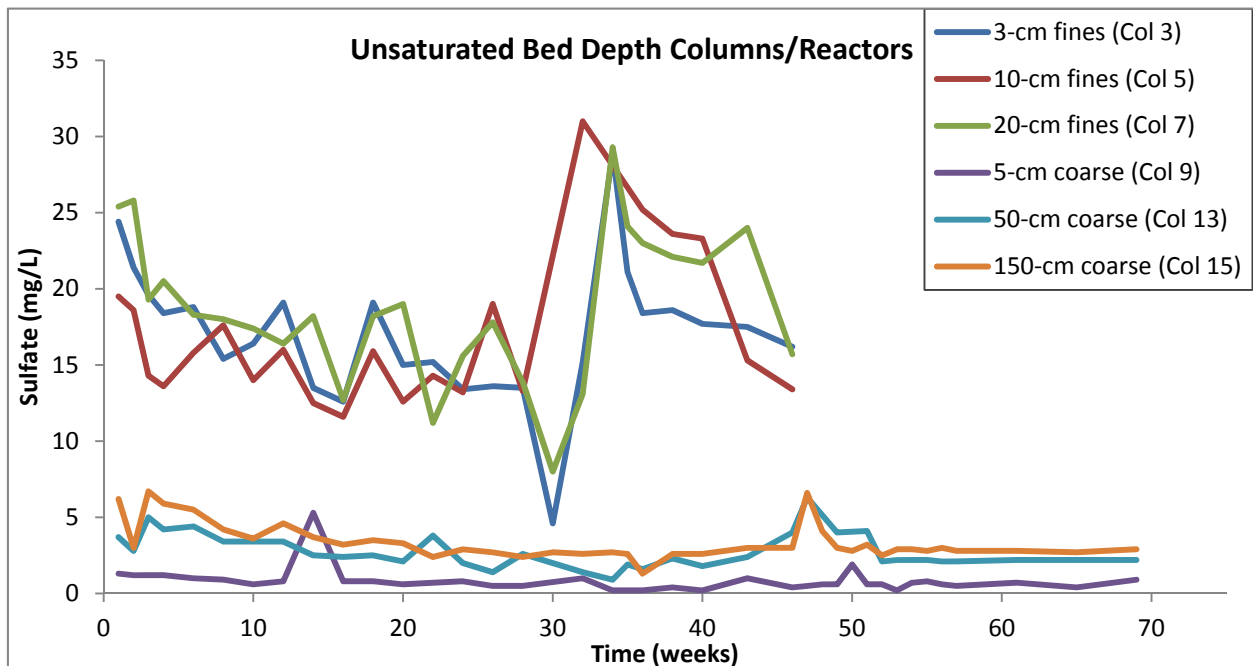
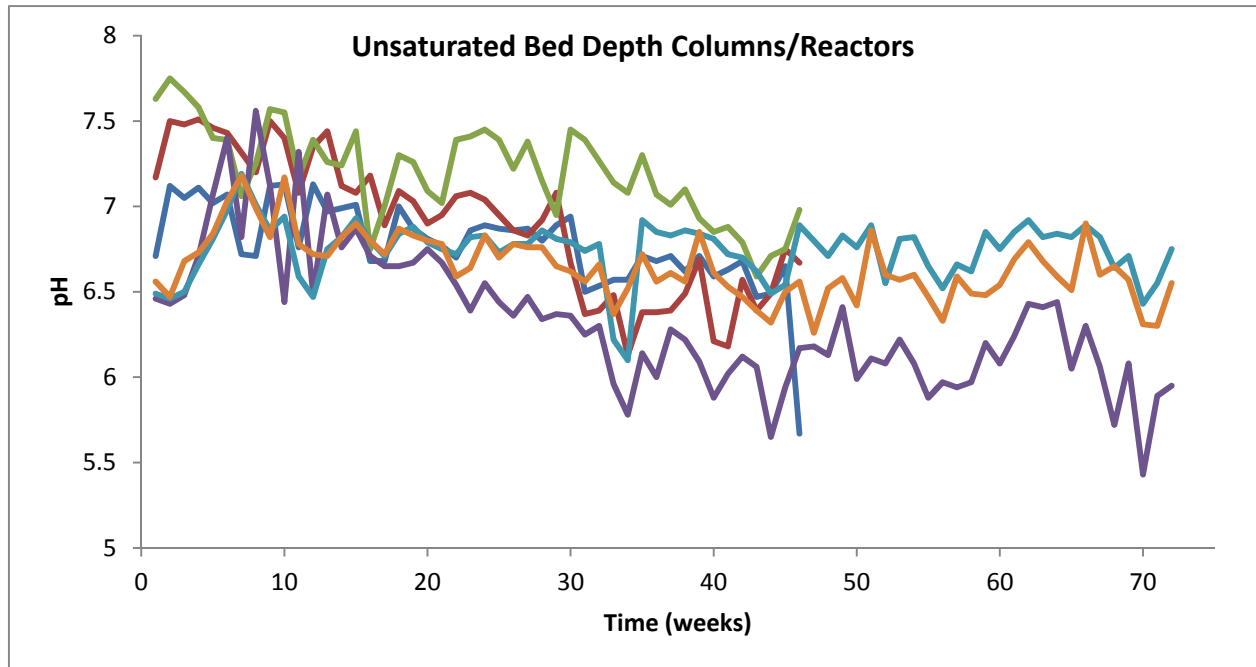


Figure 6. Observed sulfate release rates (mg/week) for the subaqueous and subaerial fine rock columns indicated oxygen diffusion limited sulfide mineral oxidation. Thus, the subaerial simulation columns likely retained significant amounts of pore water.

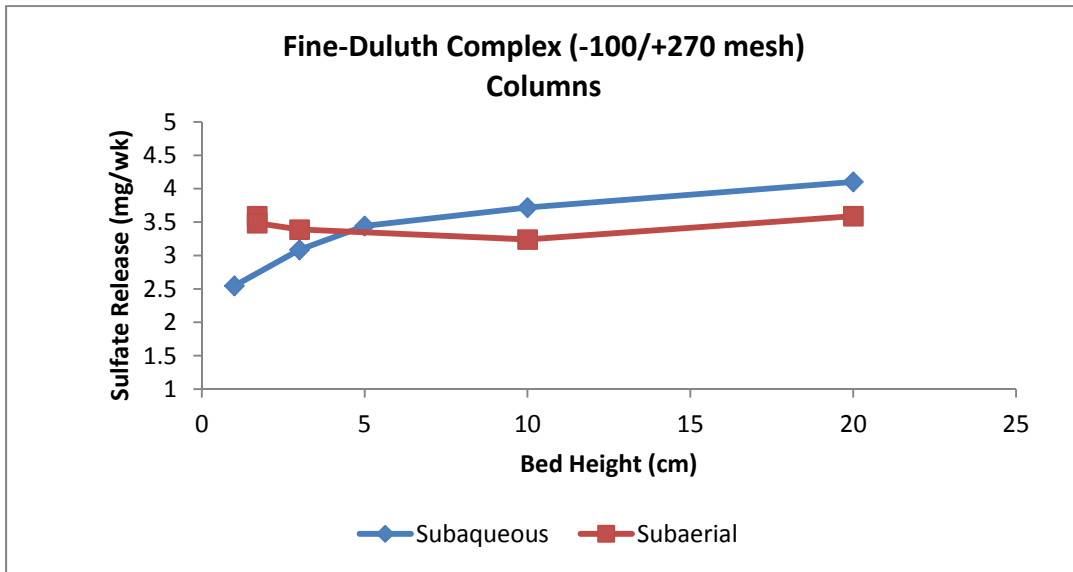
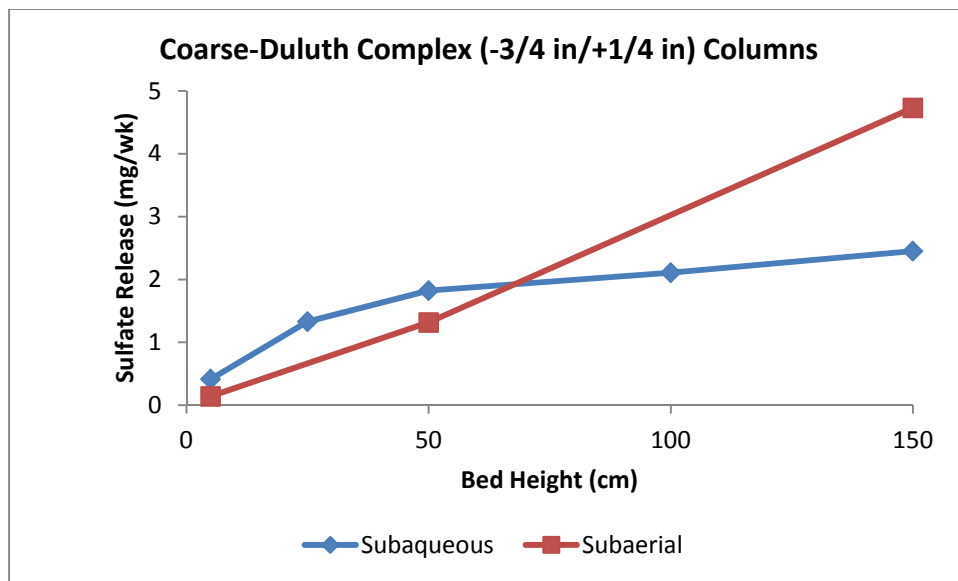


Figure 7. Sulfate release rates (mg/week) from the subaqueous coarse rock columns were similar to the subaerial columns for bed depths less than 50-cm. However, sulfate release rates for the subaqueous 150-cm bed depth was nearly half that of the subaerial simulation column.



## 5.3. Barrier Layer Column Study

### 5.3.1 . Summary of Barrier Layer Column Results

A second laboratory column experiment was initiated in March 1997 to examine the effect of placing various barriers above sulfidic waste rocks disposed in a subaqueous setting. The intent of these barriers was to further inhibit oxygen transport to the mine waste and, therefore, decrease the rate of sulfide mineral oxidation. The barriers under examination were taconite tailing, taconite tailing with an overlying layer of limestone, and taconite tailings/yard waste compost mixtures. All the barrier layer materials examined produced similar water chemistry, presented in general below. Sulfate release rates did vary with barrier layer thickness. Detailed water chemistry and sulfate release rates for each barrier layer material is presented in subsequent sections of this report:

- Subaqueous controls – section 5.3.2
- Taconite tailing barrier layer – section 5.3.3
- Tailing layer plus 1-cm limestone – section 5.3.4
- Tailing mixed with composted yard waste – section 5.3.5.

Surface and pore water pH from each of the barrier layer test columns and the two subaqueous controls remained above 6.0 throughout the 300 week period of record (Figure 8). There was little difference in pH between the subaqueous control columns and those with various barrier layers, particularly in the column pore waters. Slight differences in water cover pH with the type of barrier layer used were observed. The average water cover pH above the limestone/tailing layer averaged 8.0, which was slightly elevated in comparison to the taconite tailing layers, the composted tailing layers, and the subaqueous controls (average = 7.5, 7.5 and 7.0, respectively). In contrast, drainage pH from the subaerial control column dropped below 6.0 within 134 weeks.

As with the pH, sulfate concentration trends in the water covers and pore waters within these columns were generally independent of the type of barrier layer used above the waste rock (Figure 9). Initial sulfate concentrations in the water cover overlying the rock beds and pore waters within the rock beds were elevated for nearly 50 weeks, ranging from 70 – 140 mg/L. This was not surprising because the rock used in these columns was not rinsed to remove soluble products that accumulated on rock surfaces due to reaction prior to the onset of the experiment. During the subsequent 60 weeks of the experiment, sulfate concentrations in the water covers overlying waste rock in each of the sixteen columns decreased to less than 8 mg/L (Figure 9). Between weeks 60 and 130, sulfate levels remained low, ranging from 1-8 mg/L. Subsequently, sulfate concentrations in all columns began to increase gradually. At the end of the 298 period of record, sulfate levels for 0, 1-2, 3-4, and 5-11 cm barrier layer depths had increased to approximately 40, 27, 10 and 5 mg/L, respectively.

Initially, pore water sulfate concentrations in all sixteen columns decreased rapidly, dropping below 10 mg/L within approximately 150 weeks (Figure 9). Once these low levels were attained, pore water sulfate levels fluctuated with most values in the range of 3 – 7 mg/L for 306 weeks.

Examination of the water chemistry from each of the sixteen columns indicated that residual oxidation products on rock surfaces resulted in elevated sulfate levels in the water covers and pore waters. Consequently, the sulfate mass release during the initial weeks of the experiment reflected sulfide mineral oxidation under previous subaerial storage conditions rather than the experimental conditions, subaqueous disposal beneath a barrier layer.

In order to ensure that the sulfate mass release reflected oxidation under the desired conditions, it was necessary to estimate the mass of accumulated soluble sulfate rinsed from the waste rock during the initial phase of the experiment. In the absence of detailed solid phase sulfur analyses of the fresh waste rock, drainage quality results from the subaerial control column (#17) were examined. Sulfate concentrations in drainage from the subaerial control were initially elevated (90 mg/L) and decreased to the range of 22 – 28 mg/L within 5 weeks (Figure 10). This was determined to be the “rinse off period” and was used to approximate residual sulfate on the waste rock. At the 5 week mark, 3.4 L of water had passed through the subaerial control column or approximately three pore volumes. This corresponded to a cumulative mass of 232 mg sulfate rinsed from the waste rock (Figure 11). It was assumed that this sulfate was due to residual sulfide oxidation products rather than sulfide mineral oxidation under experimental conditions.

These values were then applied to the test columns and subsequent rate calculations. Assuming that the initial 232 mg of sulfate removed in samples from the barrier layer test columns was present on the rock at the beginning of the test, it was determined that this mass was removed in 129 – 157 weeks. This result was in good agreement with the cumulative volume of water (roughly 3 pore volumes) that had passed through the barrier layer test columns and the observed decrease in pore water sulfate concentrations up to that point. Thus, a conservative rate period estimate from 144 to 306 weeks was used to identify the period of sulfide mineral oxidation and release to the water cover under the desired test conditions.

Examination of the pore water chemistry in the barrier layer test columns over the period of 157 – 306 weeks showed that sulfate concentrations stabilized at roughly 5 mg/L (Figure 9) Sulfate mass release was fairly constant, indicating steady state conditions were approximated within the waste rock beds. Thus, the contribution of sulfate from sulfide mineral oxidation at depth was determined to be negligible. Consequently, sulfide mineral oxidation rates in this presentation were calculated based on the sulfide mass release to the water cover for the period of time between weeks 144 and 298 (Table 8, Figures 18, 22 and 26). The complete set of rate calculations can be found in Appendix D.

Figure 8. Surface and pore water pH for subaqueous Duluth Complex waste rock with barrier layers remained above 6.0 throughout the experiment. Subaqueous control pH values (black lines) were slightly lower than the barrier layers, but remained above 6.0. Pore water sample size was decreased to 5 mL after week 130 and pH was not determined.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

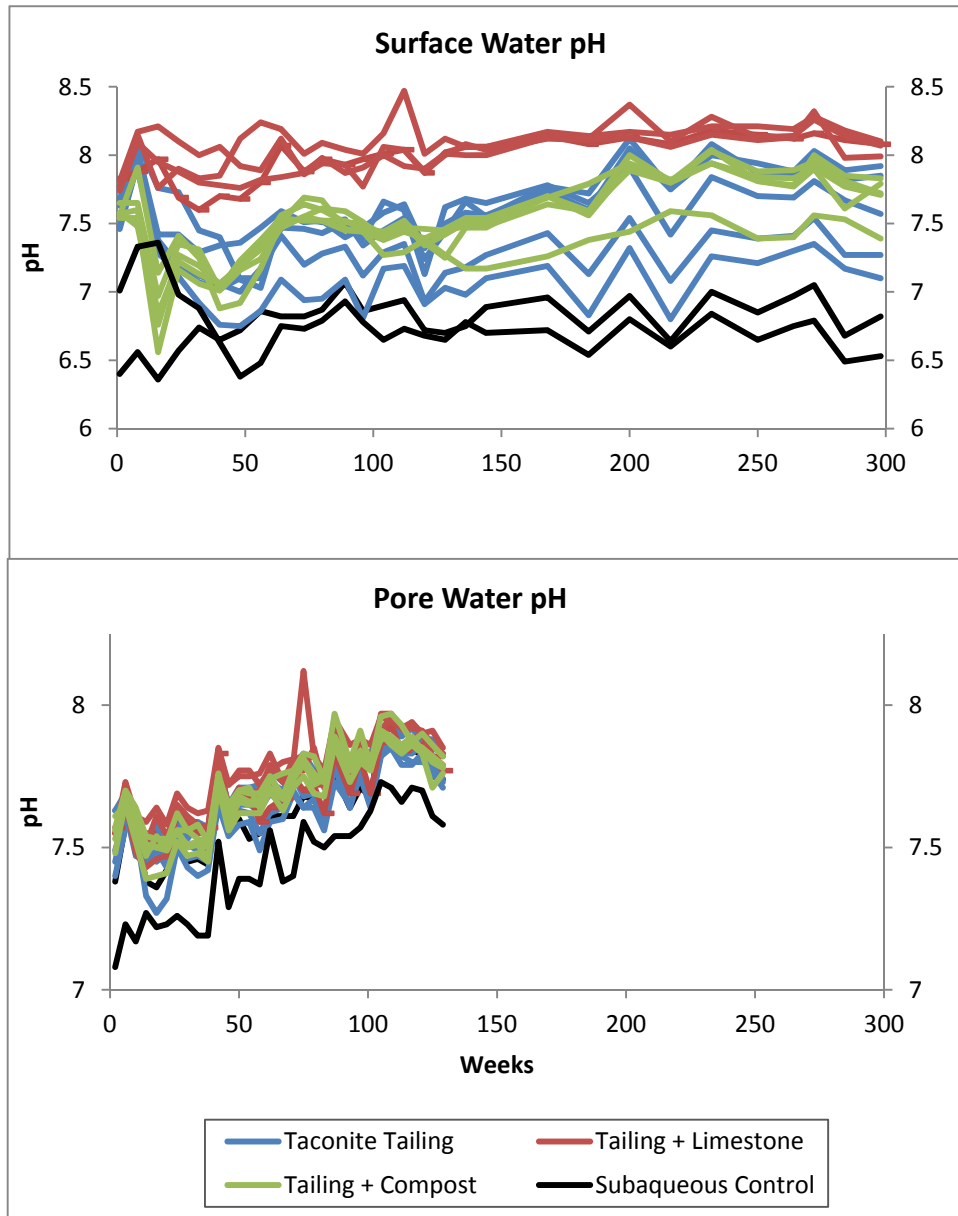


Figure 9. Sulfate concentrations in the column water cover layers and pore waters were consistent regardless of the barrier layer material used (taconite tailings, limestone, compost). Only barrier layer depths of 0 – 11 cm are depicted here.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

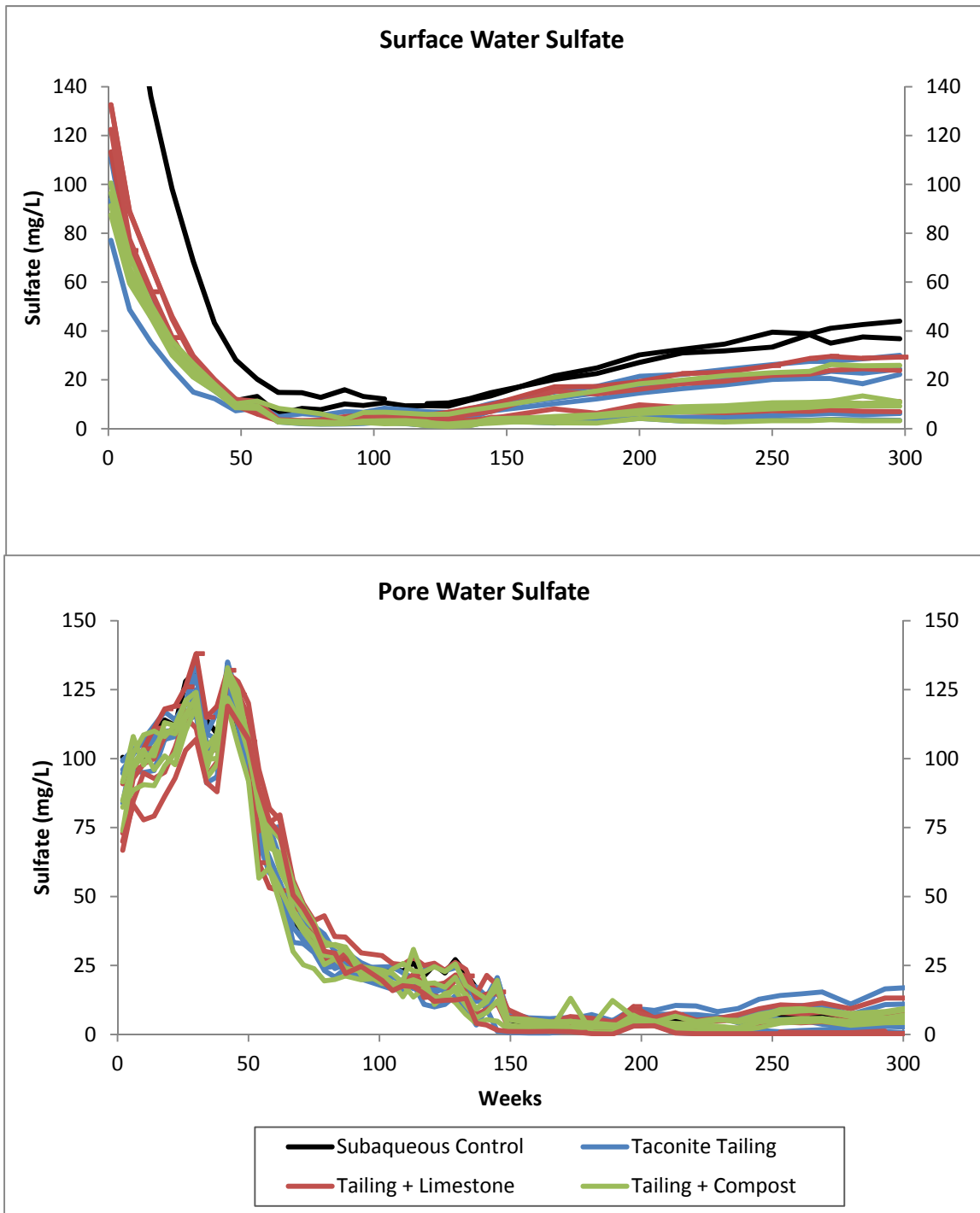




Figure 10. Drainage chemistry from the subaerial rock control (Column 17) was used to estimate the mass of residual soluble sulfate rinsed from rock surfaces during the initial five weeks of the experiment.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

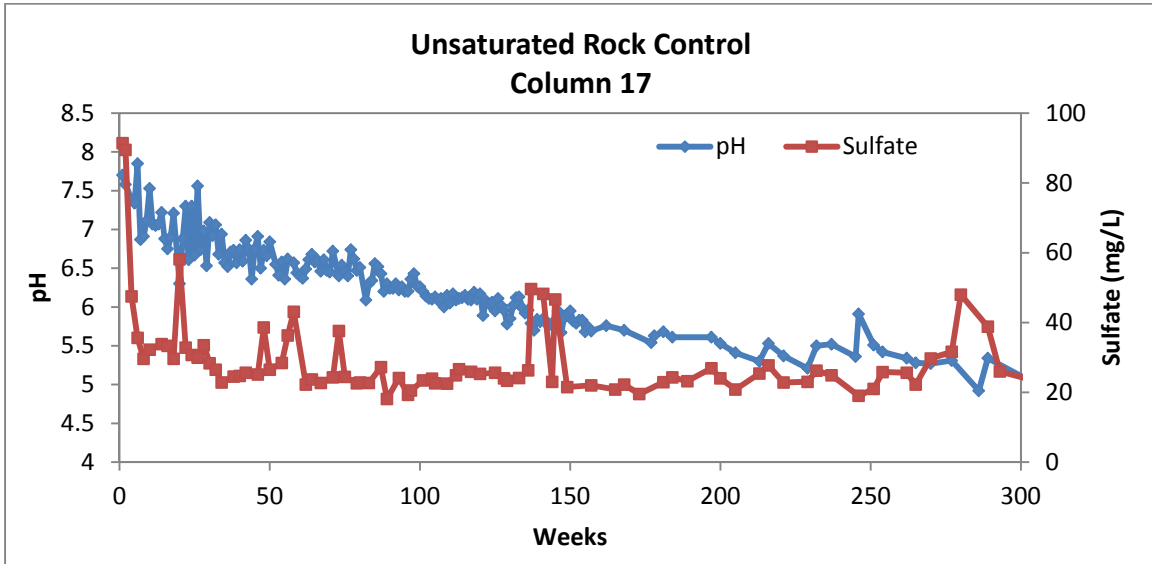


Figure 11. Based on sulfate mass release from the subaerial control column (17), it was determined that residual oxidation products were effectively removed after three pore volumes of water had passed through the rock bed.

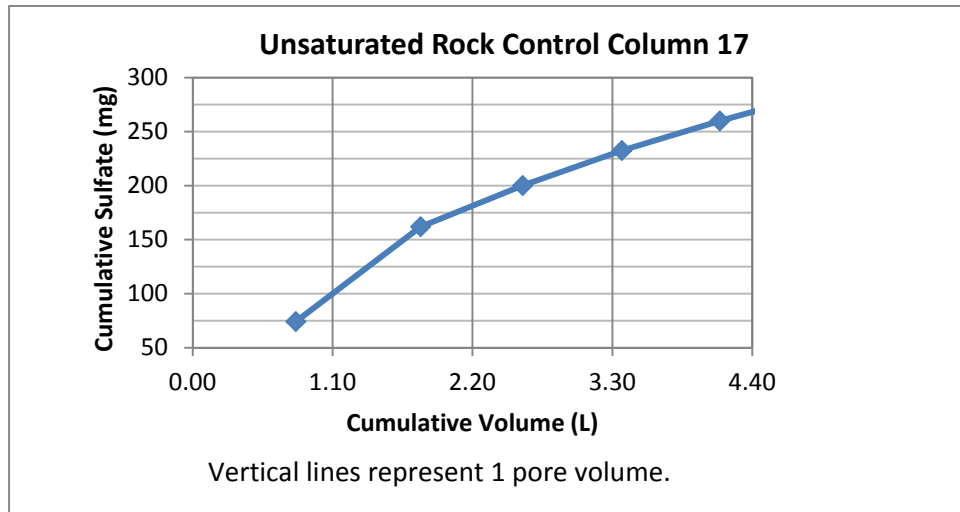


Table 8. Summary of sulfate release rates (mg/week). In general, sulfate release rates decreased as the barrier layer depth increased for all types of barrier layers tested in this study: taconite tailing, taconite tailing and limestone, and taconite tailing mixed with composted yard waste.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

Barrier Layer Depth (cm)	Sulfate Release Rates (mg/week)			
	Subaqueous Controls	Taconite Tailing	Taconite Tailing + Limestone	Taconite Tailing with Compost
0	0.62			
1		0.46	0.45	0.41
2		0.39	0.37	
3		0.34		0.17
4			0.17	
5		0.10		
10		0.07		0.07
11			0.13	

### 5.3.2. Subaqueous Controls (Columns 1 & 2)

Control columns using unscreened ( $< 19$  mm, column 1) and screened ( $1.40 \leq d \leq 4.75$  mm, column 2) rock were used to simulate waste rock disposed of in a subaqueous environment without a barrier layer. In both control columns, pH levels remained above the water quality standard of 6.0 for 300 weeks, averaging 7.0 and 7.5 in the water cover and pore water, respectively (Figures 12 and 13).

Initial sulfate concentrations in the water cover over the unscreened rock bed were two to three times higher than those of the screened rock (Figure 12). However after 48 weeks (approximately one pore volume of water passing through the columns), sulfate concentrations were in good agreement between the two columns. Sulfate levels in the water covers of the two subaqueous control columns plateaued at 10 - 15 mg/L until week 144, when they gradually began to increase reaching 40 mg/L at the end of the experiment (298 weeks).

Pore water sulfate concentrations increased during the first 30 weeks of the experiment, reaching 300 mg/L in the unscreened rock control and 130 mg/L in the screened rock control (Figure 13). This was presumably due to the rinsing off of residual oxidation products from rock surfaces. Sulfate levels decreased rapidly until about week 90, at which point sulfate concentrations from both the unscreened and screened rock controls were in good agreement. After an estimated three pore volumes of water had passed through the columns, sulfate concentrations became fairly constant at roughly 5 – 10 mg/L.

Cumulative sulfate release from the unscreened rock control was approximately two times higher than that observed in the screened rock control (Figure 14). Much of this difference was the result of elevated sulfate release from the unscreened rock during the rinsing of residual reaction products. After the approximately three pore volumes of water had passed through the columns, sulfate release rates from the unscreened and screened rock were in good agreement at 0.57 and 0.67 mg/week, respectively (Table 9, section 4.5.2). This indicates that limiting rock used in the experiment to the screened fraction ( $+14/-4$  mesh or equivalently  $1.19 < d < 4.76$  mm) did not result in rates that were substantially different from unscreened rock.

Figure 12. Water chemistry in the two (unscreened and screened rock) subaqueous controls replicated well subsequent to removal of residual oxidation products. Surface water pH levels remained above 6.0. Sulfate concentrations in the water cover waters had reached approximately 40 mg/L at 298 weeks.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

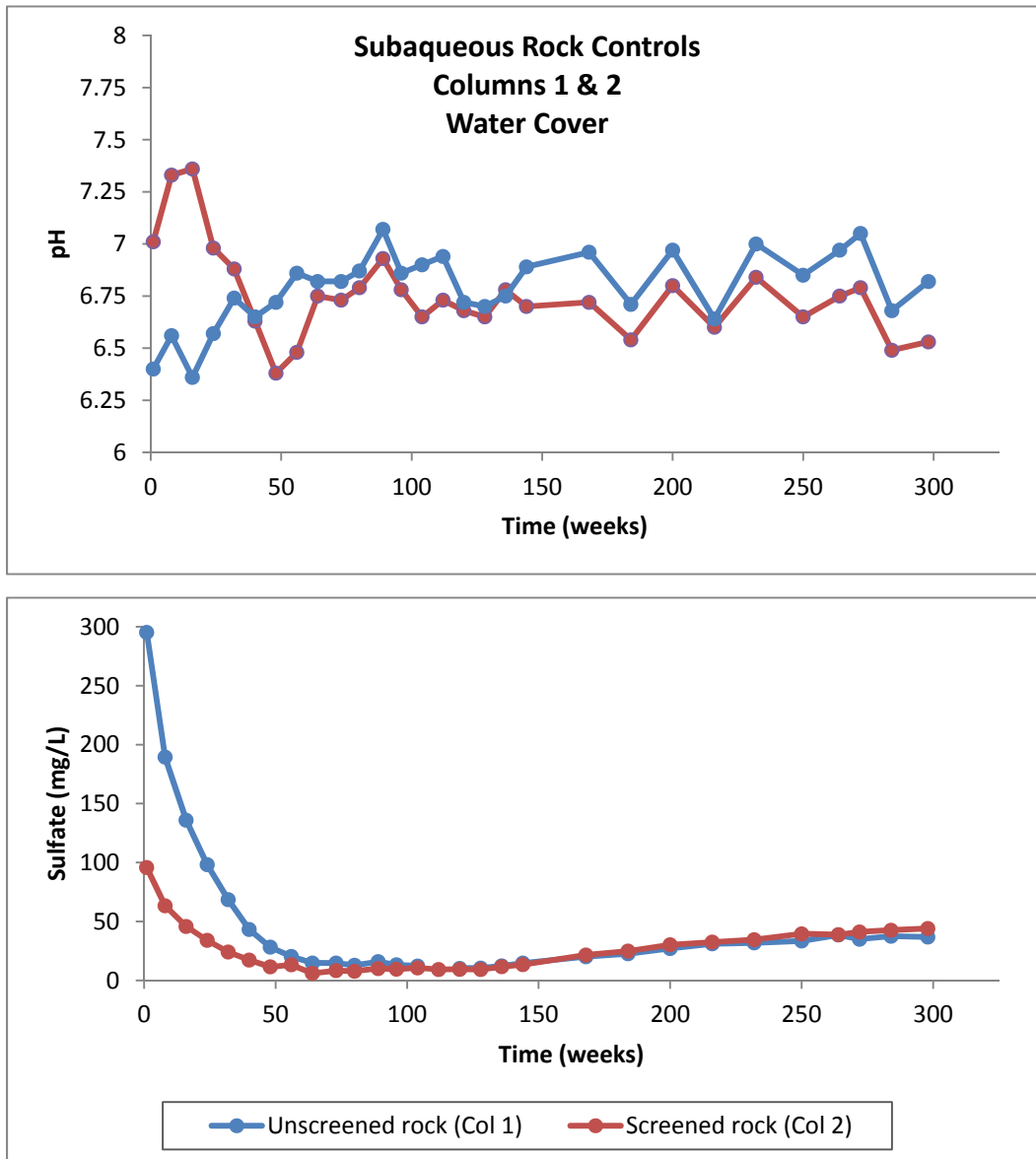


Figure 13. Water chemistry in the two (unscreened and screened rock) subaqueous controls replicated well subsequent to removal of residual oxidation products. Pore water pH levels remained above 6.0. Sulfate concentrations in the pore waters reached a steady state of approximately 5-10 mg/L between weeks 157 and 306.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

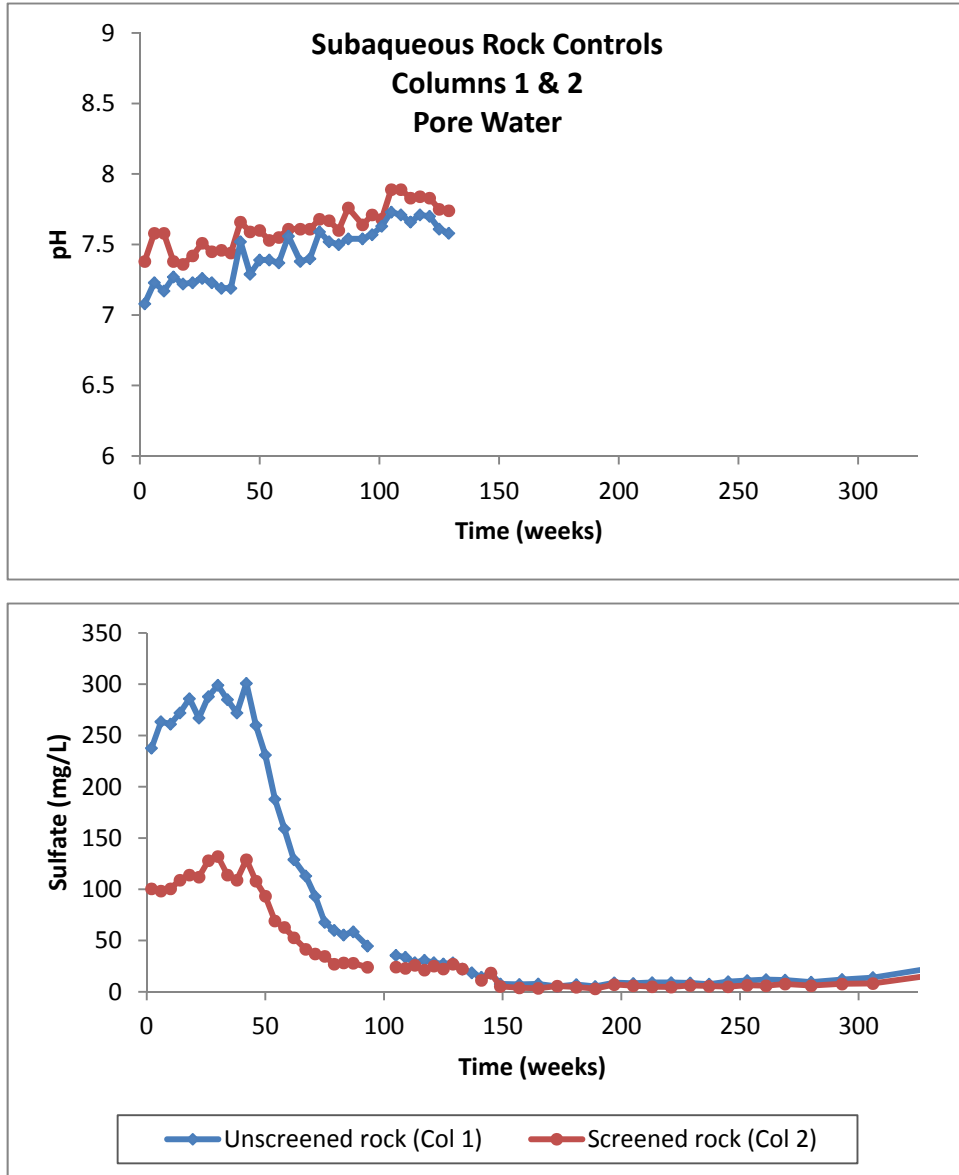


Figure 14. Cumulative sulfate release from barrier layer columns containing Duluth Complex waste rock. After approximately 150 weeks, sulfate release to the pore waters was negligible. However increasing sulfate mass release to the water cover indicated some sulfide mineral oxidation was still occurring.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

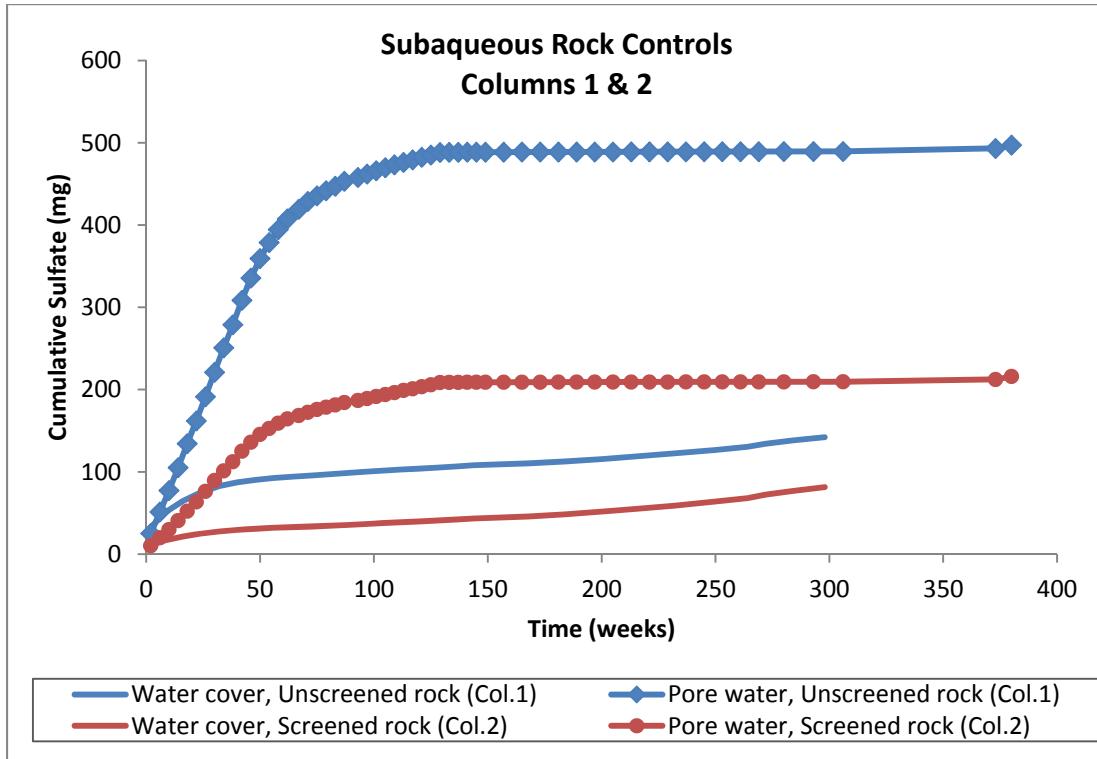


Table 9. Sulfate release rates in the two subaqueous control columns were in good agreement, but higher than predicted under oxygen transport limited conditions.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

	Rate Period (weeks)	Sulfate Release Rate [mg/week]	
		Unscreened Rock (Column 1)	Screened Rock (Column 2)
Water Cover	144 – 298	0.57	0.666
Pore Water	157 – 306	0.05	0.025
Overall		0.62	0.69

### 5.3.3. Taconite Tailing Barrier Layer (Columns 3, 4, 5, 6, & 7)

Taconite tailings were used as an oxygen transport barrier above sulfidic waste rock disposed of in a subaqueous environment. Tailing bed depths of 1, 2, 3, 5 and 10 cm were tested. In all five tailing layer columns, the pH of the water covers and pore waters remained above the water quality standard of 6.0 (Figures 15 and 16). Average pH values of the water covers increased somewhat with the depth of the tailing barrier, perhaps due to dissolution of small amounts of carbonate minerals in the tailings (Table E1.3). Pore water pH was reasonably stable at 7.7.

Initial sulfate concentrations in the water covers ranged from 77 to 111 mg/L (Figure 15). During the 48 weeks of sampling, sulfate concentrations decreased rapidly to less than 10 mg/L. Sulfate levels in the water covers plateaued at 2 - 7 mg/L until week 130, when they gradually began to increase. At the end of 298 weeks, sulfate levels in the water covers over the 1, 2, 3, 5, and 10-cm depth tailing beds reached 30, 24, 22, 6, and 3 mg/L, respectively.

Pore water sulfate concentrations increased during the first 42 weeks of the experiment, reaching approximately 135 mg/L (Figure 16). Sulfate levels decreased rapidly until about week 80, at which point sulfate concentrations began to decrease more slowly. After approximately 133 weeks, sulfate concentrations became fairly constant at roughly 5 – 10 mg/L.

Cumulative sulfate release to the water covers ranged from approximately 30 mg for the 10-cm thick tailing barrier to nearly 90 mg in the 1-cm tailing barrier (Figure 17). Correcting the sulfate mass release to the pore water for the mass attributed to residual sulfide oxidation products (232 mg), resulted in negligible sulfate release to pore waters. During the period of time assumed to represent sulfide mineral oxidation beneath a layer of taconite tailing in subaqueous conditions, sulfate release rates were observed to decrease as the depth of taconite tailing used in the barrier layer increased (Figure 18). Observed sulfate release rates to the water cover were 0.46, 0.39, 0.34, 0.10, and 0.07 mg/week for the 1, 2, 3, 5, and 10-cm depth barrier layers, respectively (Table 10, section 4.5.2).

Figure 15. The bed depth of taconite tailing barrier layers did not significantly affect pH or sulfate concentrations in the water covers. At the end of 298 weeks, sulfate concentrations were highest in the water cover above the 1-cm tailing barrier layer.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

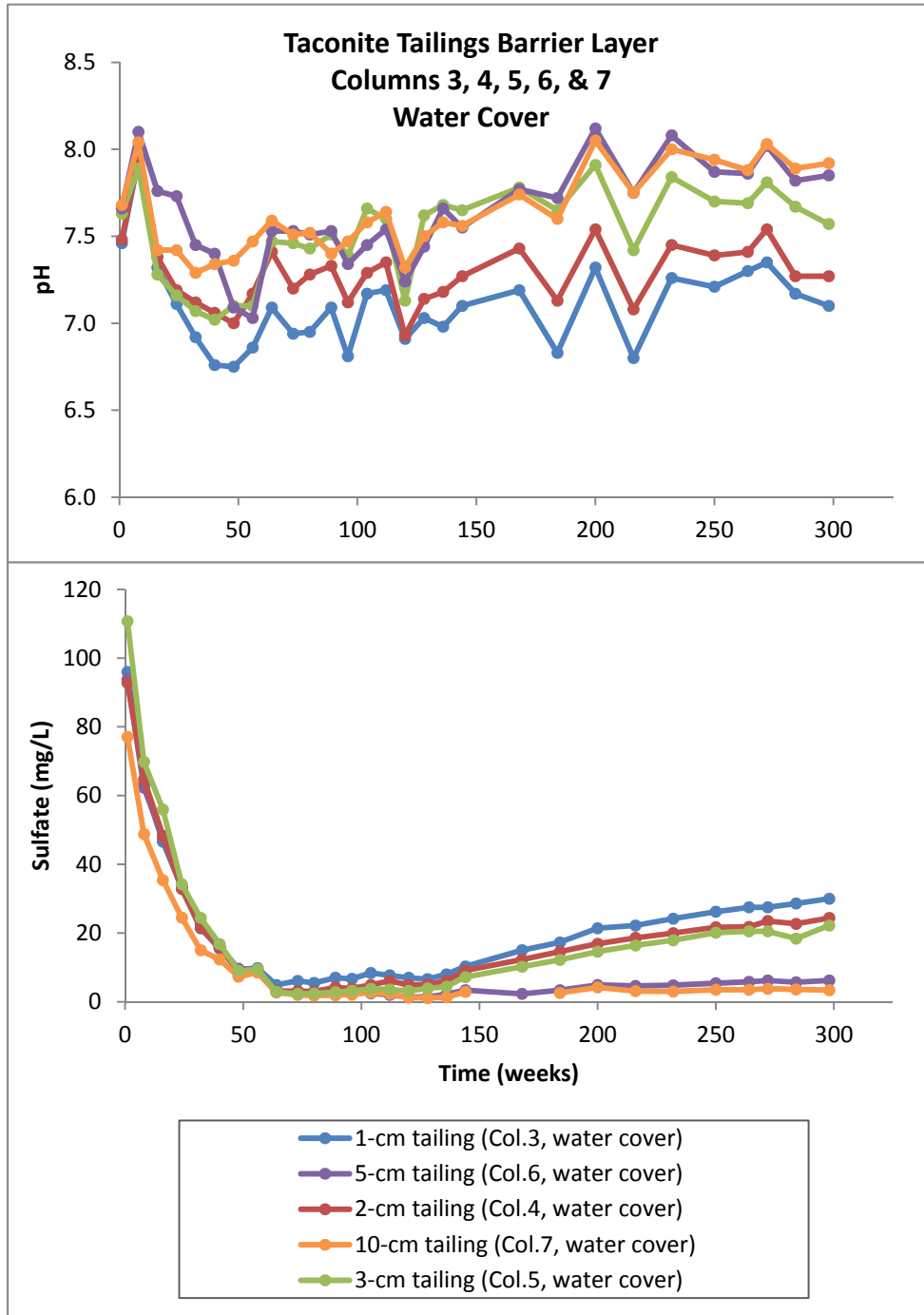




Figure 16. The bed depth of taconite tailing barrier layers did not significantly affect pH or sulfate concentrations in the column pore waters. Between weeks 157 and 306, sulfate concentrations remained fairly stable at 5-10 mg/L. Sample volumes were reduced to 5 mL after week 130, therefore pH could not be measured.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

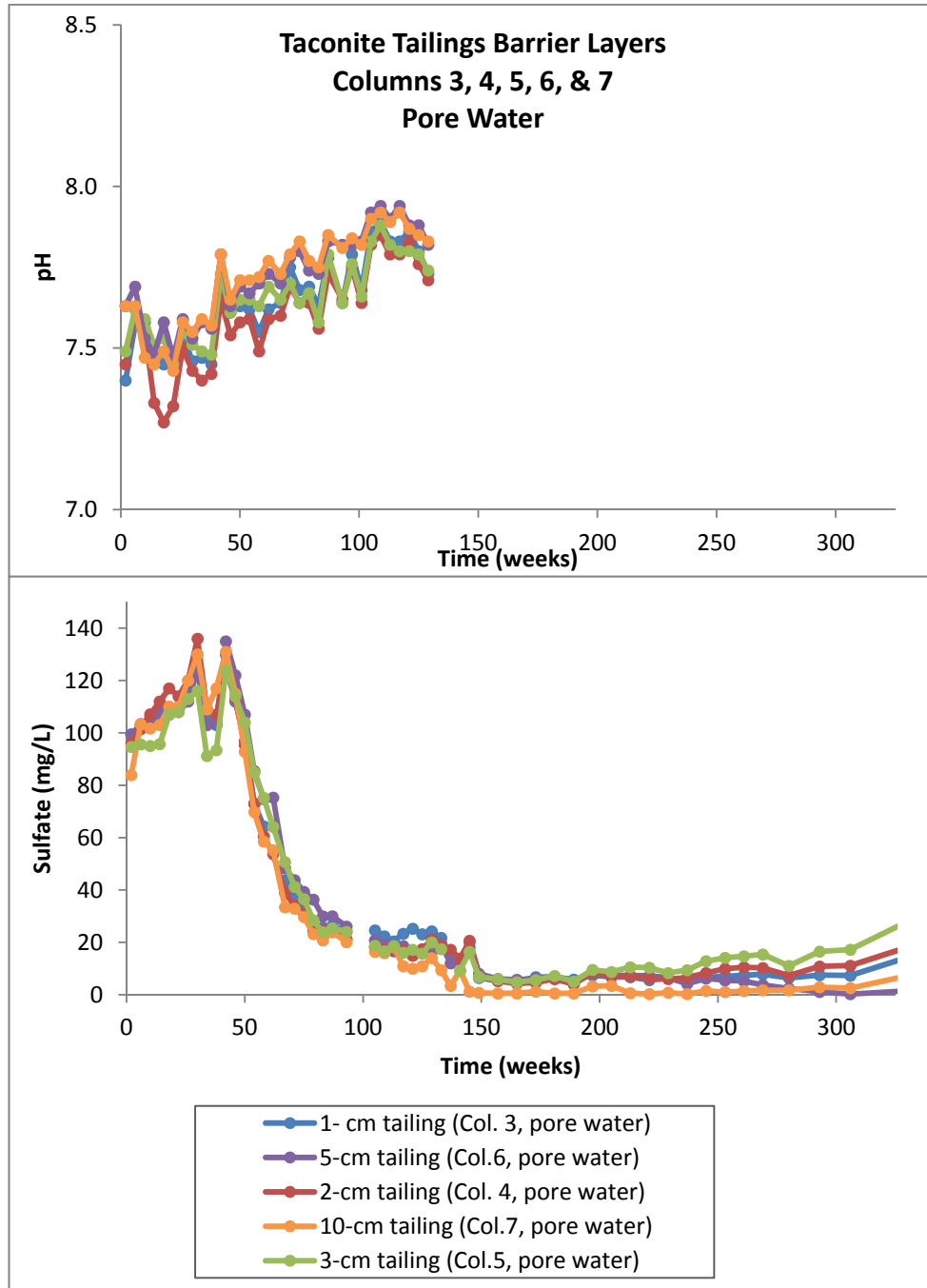


Figure 17. Cumulative sulfate release from subaqueous Duluth Complex waste rock beneath a layer of taconite tailing. Sulfate mass release to the water cover for the 10-cm thick taconite tailing layers was approximately one third that of the 1-cm thick layer. Sulfate mass release to the waste rock pore waters was fairly constant, indicating steady state conditions.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

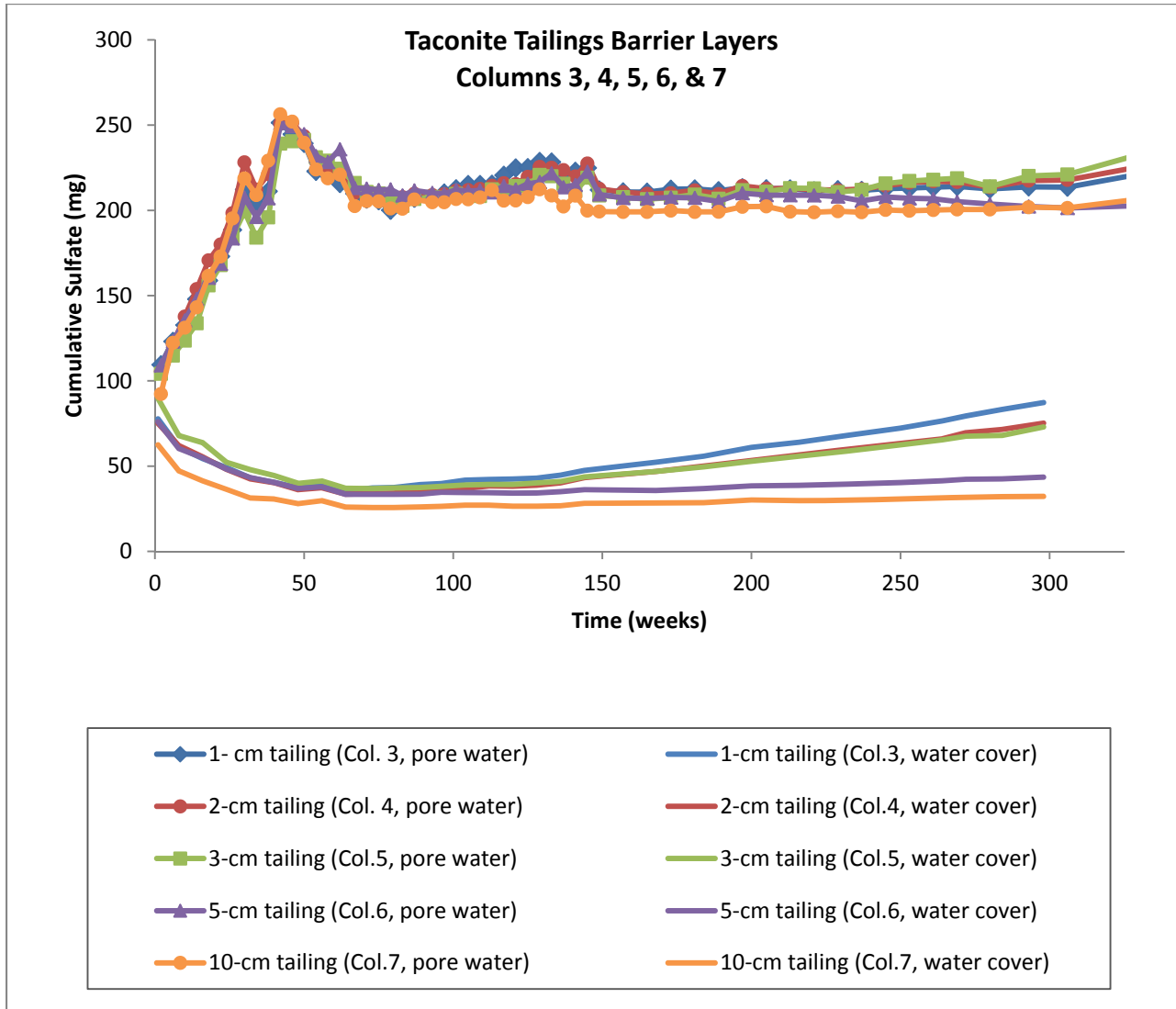


Figure 18. The 5- and 10-cm taconite tailing barrier layers reduced sulfate release rates to roughly 20% of those observed in the subaqueous control columns (depth = 0-cm).

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

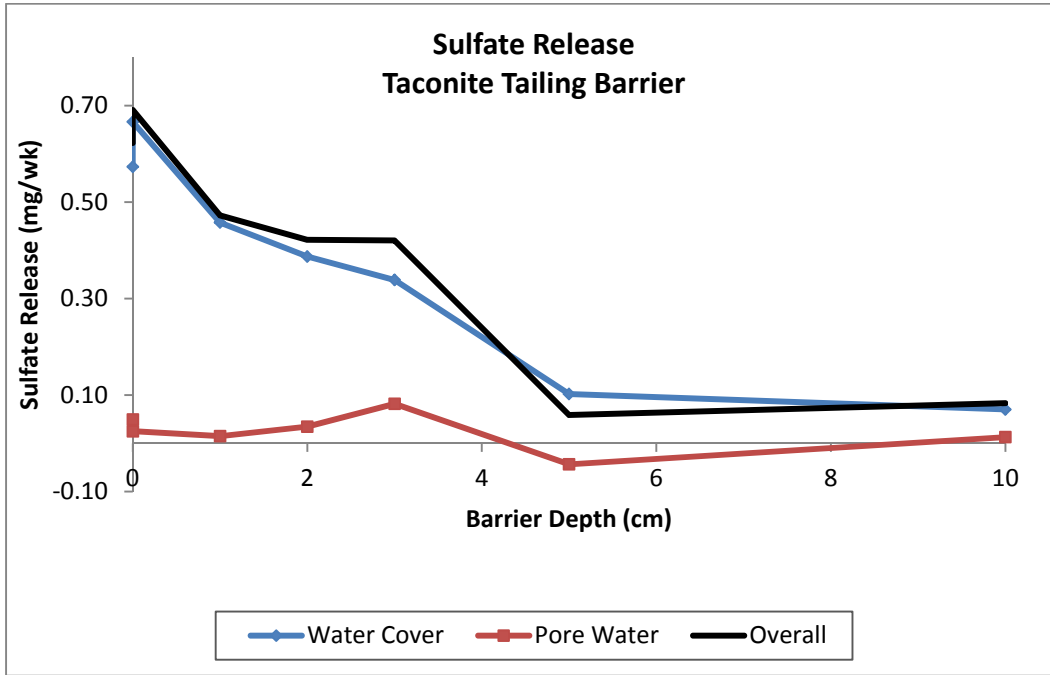


Table 10. Sulfate release rates to the water cover decreased as the depth of the taconite tailing barrier layer increased.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

	Rate Period (weeks)	Sulfate Release Rate [mg/week]				
		Column 3 1-cm tailing	Column 4 2-cm tailing	Column 5 3-cm tailing	Column 6 5-cm tailing	Column 7 10-cm tailing
<b>Water Cover</b>	<b>144 – 298</b>	<b>0.46</b>	<b>0.39</b>	<b>0.34</b>	<b>0.10</b>	<b>0.070</b>
Pore Water	157 – 306	0.015	0.035	0.082	-0.044	0.013
Overall		0.47	0.42	0.42	0.06	0.08

#### **5.3.4. Taconite Tailings and Limestone Barrier Layers**

**(Columns 8, 9, 10 & 11)**

Taconite tailings with an additional acid neutralizing layer of limestone were used to simulate an oxygen transport barrier above sulfidic waste rock disposed of in a subaqueous environment. Tailing bed depths of 0, 1, 3, and 10-cm with an overlying 1-cm layer of limestone were tested. At all tailing/limestone barrier layer depths, the pH of the water cover and pore waters gradually increased to approximately 8, due to the additional alkalinity provided by the limestone (Figures 19 and 20).

Initial sulfate concentrations in the water covers ranged from 113 to 133 mg/L (Figure 19). During the initial 48 weeks, sulfate concentrations decreased rapidly to less than 7 mg/L. Sulfate levels in the water covers plateaued at 3 - 6 mg/L until week 130, when they gradually began to increase again. At the end of 298 weeks, sulfate levels in the water covers over the 0, 1, 3, and 10-cm depth tailing with 1-cm limestone beds had reached 29, 24, 11, and 7 mg/L, respectively.

Pore water sulfate concentrations increased during the first 42 weeks of the experiment, reaching approximately 130 mg/L (Figure 20). This was presumably due to the rinsing off of residual oxidation products from rock surfaces. That is, the distribution of sulfate concentrations was likely affected by the method of water addition to saturate the column. Water was added from the bottom up, which may have created a maximum sulfate concentration near the surface (section 4.2.2). These concentrations are similar to those initially observed in the water cover. Sulfate levels decreased rapidly until about week 80, at which point sulfate concentrations began to decrease more slowly. After an estimated three pore volumes of water had passed through the columns (133 weeks), sulfate concentrations became fairly constant at values less than 6 mg/L. No samples were taken between weeks 306 and 373 which resulted in an accumulation of sulfate in the pore waters. Thus, final sulfate concentrations ranging from 3 – 65 mg/L were observed just prior the conclusion of the experiment.

Cumulative sulfate release to the water covers ranged from approximately 52 mg for the 11-cm thick tailing-limestone barrier to nearly 86 mg in the 1-cm limestone barrier (Figure 21). Correcting the sulfate mass release to the pore water for the mass attributed to residual sulfide oxidation products, resulted in negligible sulfate release to the pore waters (Figure 22). During the period of time assumed to represent sulfide mineral oxidation beneath a subaqueous layer of taconite tailing and 1-cm limestone, sulfate release rates were observed to decrease as the depth of taconite tailing used in the barrier layer increased (Figure 22). Observed sulfate release rates to the water cover were 0.45, 0.37, 0.17, and 0.13 mg/week for the 1, 2, 4, and 11-cm depth barrier layers, respectively (Table 11, section 4.5.2).

Figure 19. The addition of a 1-cm limestone layer above the taconite tailing layer raised pH of the water covers to approximately 8.0. Sulfate concentrations reached 29, 24, 10, and 7 mg/L for the 1-, 2-, 4-, and 11-cm thick barrier layers after 298 weeks.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

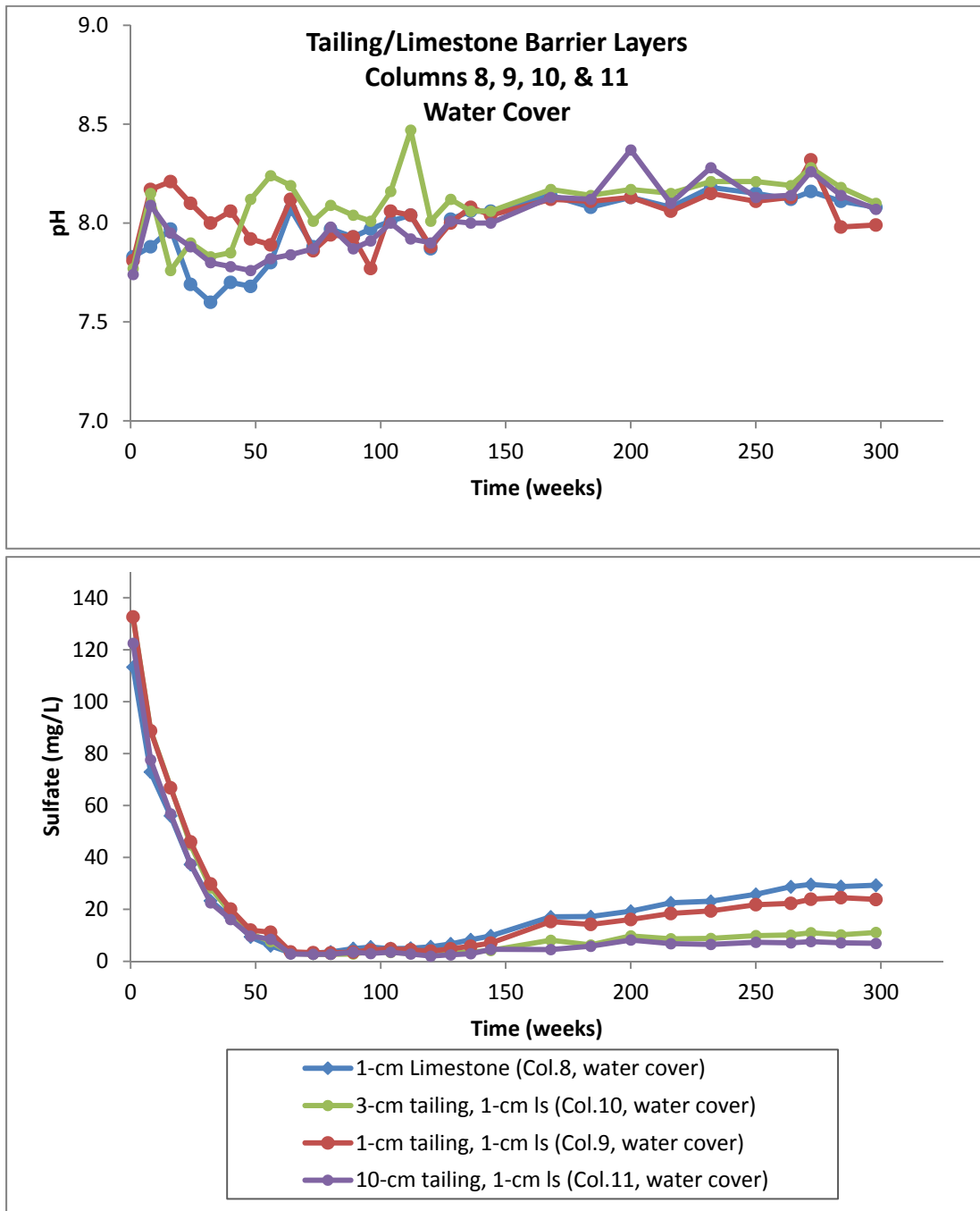


Figure 20. The addition of a 1-cm limestone layer above the taconite tailing layer raised pH of the pore waters to approximately 8.0. Pore water sulfate concentrations plateaued at less than 15 mg/L between weeks 157 and 306. These sulfate concentrations were similar to those observed in the columns with taconite tailings alone and taconite tailings mixed with 0.1 – 1% compost.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

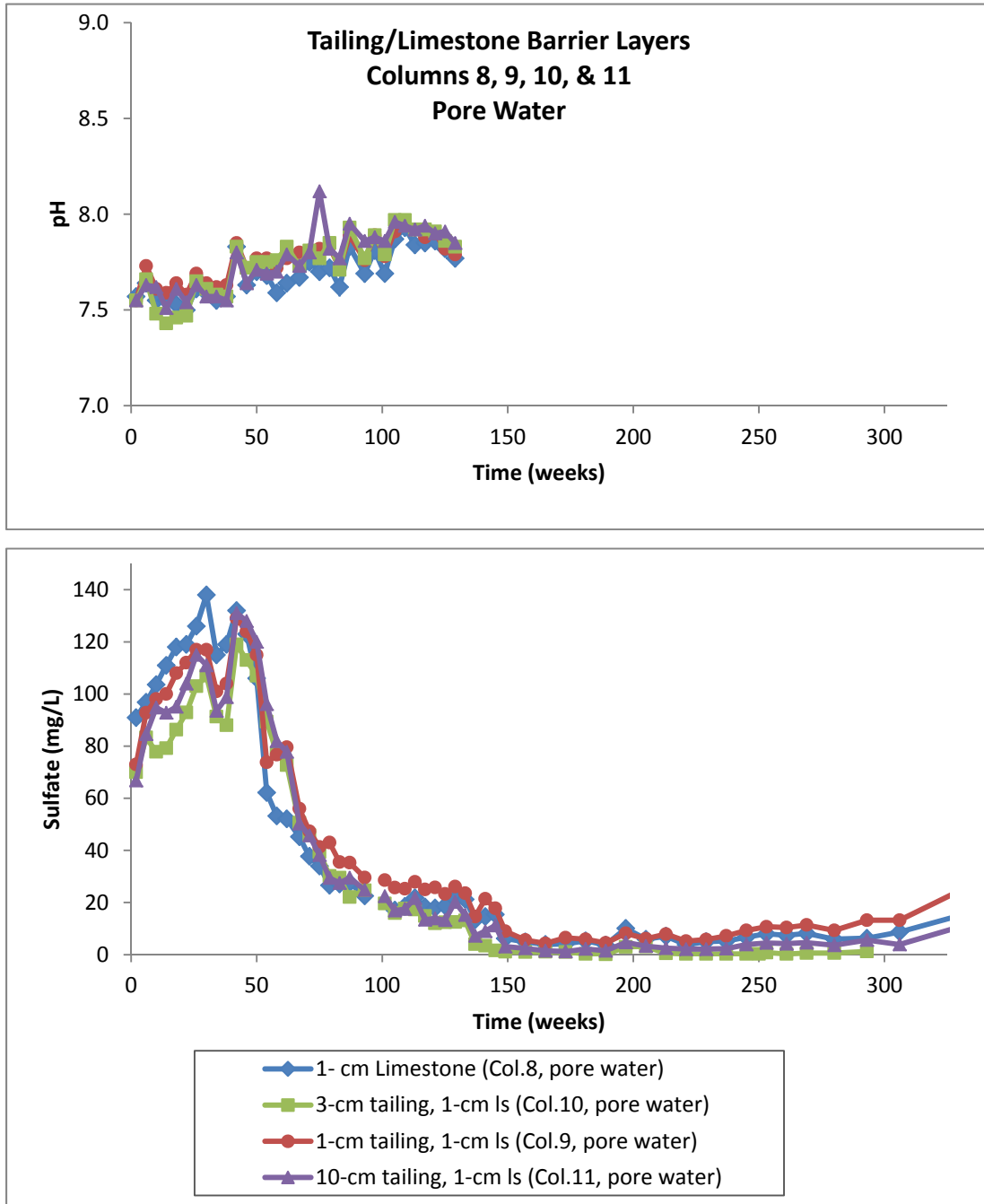


Figure 21. Cumulative sulfate release from subaqueous Duluth Complex waste rock beneath a layer of taconite tailing and 1-cm limestone. Sulfate mass release to the water cover for the 11-cm thick layer was approximately two thirds that of the 1-cm thick layer. Sulfate mass release to the waste rock pore waters was fairly constant, indicating steady state conditions.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

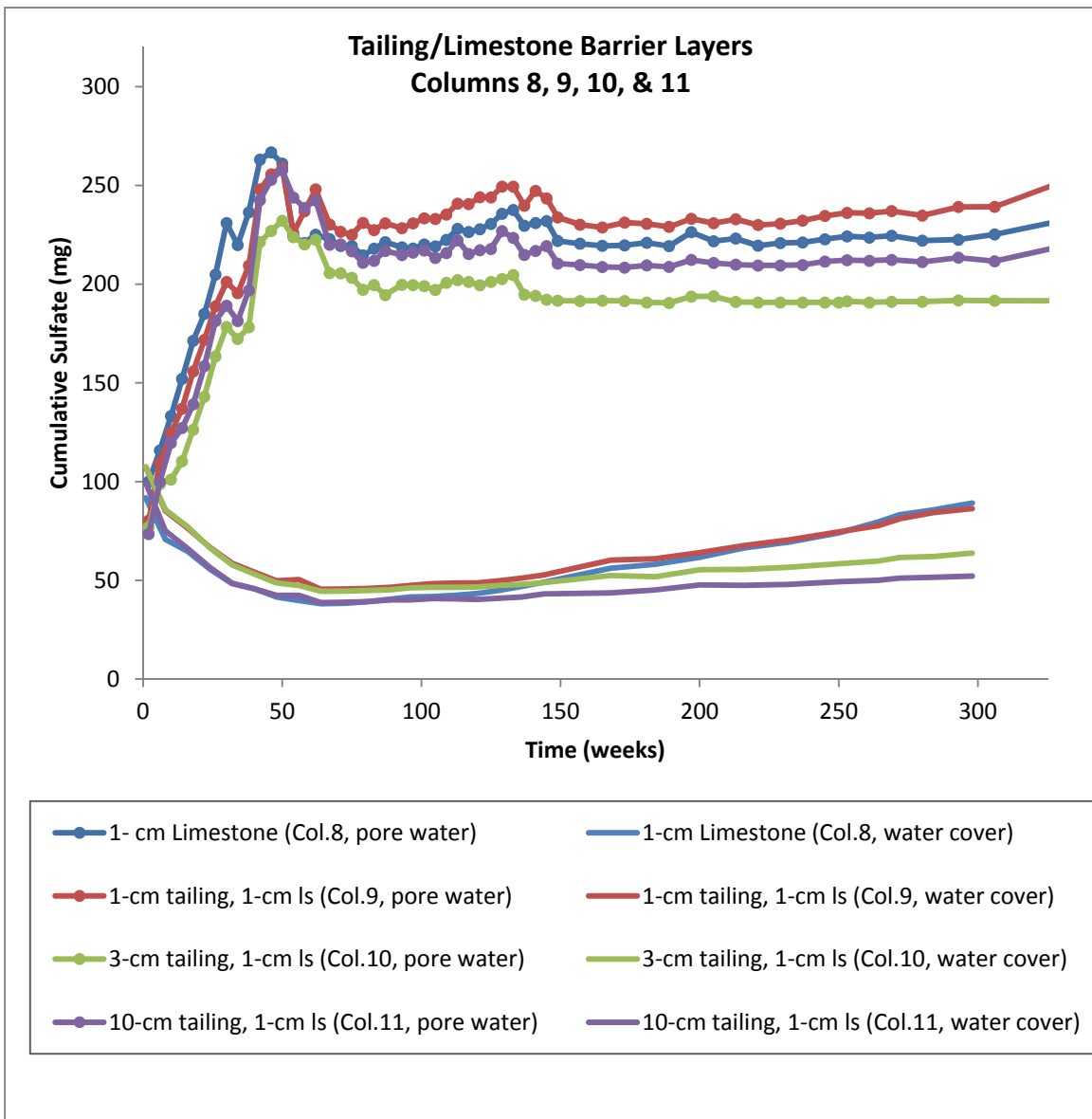


Figure 22. The 3- and 10-cm taconite tailing barrier layers with 1-cm limestone (total depths 4 and 11 cm) reduced sulfate release rates to 20 – 25% of those observed in the subaqueous control columns (depth = 0-cm).

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

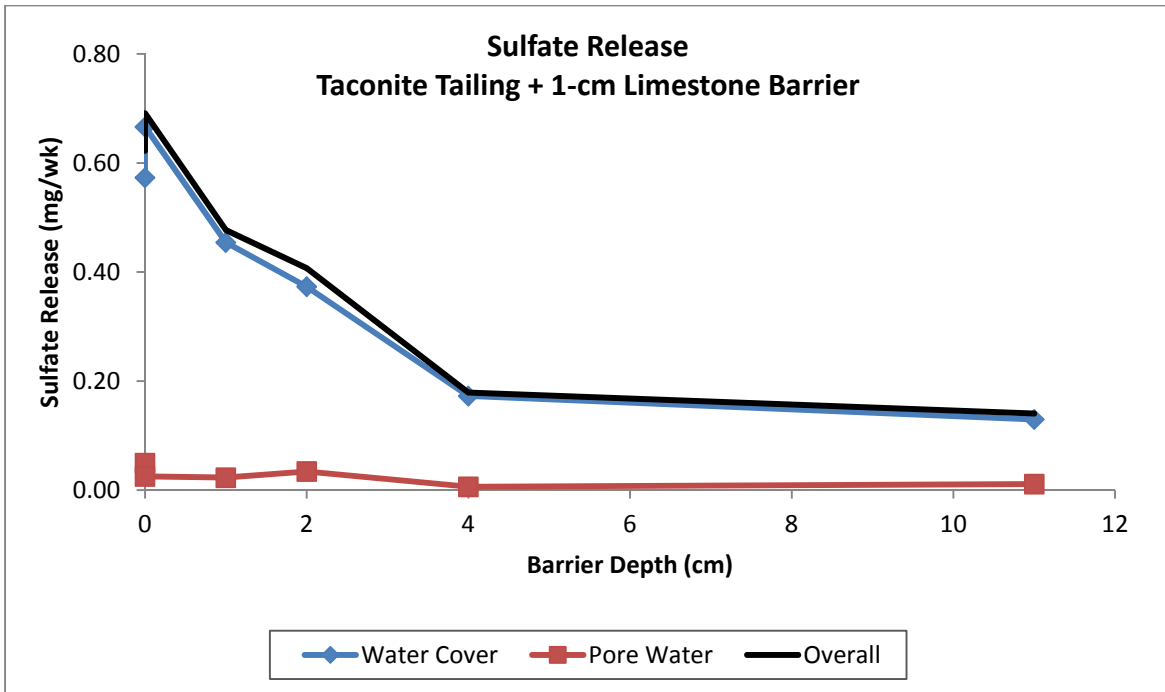


Table 11. Sulfate release rates to the water cover decreased as the depth of the taconite tailing barrier layer with an overlying layer of 1-cm limestone increased.

Rate Period (weeks)	Rate	Sulfate Release Rate [mg/week]			
		Column 8 0-cm tailing 1-cm limestone	Column 9 1-cm tailing 1-cm limestone	Column 10 3-cm tailing 1-cm limestone	Column 11 10-cm tailing 1-cm limestone
Water Cover	144 – 298	0.45	0.37	0.17	0.13
Pore Water	157 – 306	0.023	0.034	0.006	0.011
Overall		0.48	0.41	0.18	0.14



### 5.3.5. Taconite Tailings and Compost Barrier Layers (Col. 12, 13, 14, 15, & 16)

Layers of taconite tailings mixed with composted yard waste were used to simulate an oxygen-consuming and transport barrier above sulfidic waste rock disposed of in a subaqueous environment. Tailing bed depths of 1, 3, and 10-cm with 0.1% compost were tested. Two additional columns using the 3-cm tailing depth with 0.5% and 1% compost were also tested. The pH of the water cover and pore waters in all five columns generally increased over time, reaching the upper 7's in 300 weeks (Figures 23 and 24).

Initial sulfate concentrations in the water covers ranged from 88 to 100 mg/L (Figure 23). During the initial 48 weeks, sulfate concentrations decreased rapidly to less than 7 mg/L. Sulfate levels in the water covers plateaued at 3 - 6 mg/L until week 130, when they gradually began to increase again. At the end of 298 weeks, sulfate levels in the water covers over the 1, 3, and 10-cm depth tailing with 0.1% compost had reached 26, 11, and 3 mg/L, respectively. Sulfate concentrations in pore waters beneath the 3-cm tailings layers mixed with 0.1%, 0.5% and 1% compost were in good agreement, ranging from 9 - 11 mg/L, at 298 weeks.

Pore water sulfate concentrations increased during the first 42 weeks of the experiment, reaching 120 - 130 mg/L (Figure 24). This was presumably due to the rinsing off of residual oxidation products from rock surfaces. Sulfate levels decreased rapidly until about week 80, at which point sulfate concentrations began to decrease more slowly. After an estimated three pore volumes of water had passed through the columns (133 weeks), sulfate concentrations became fairly constant, averaging 5 mg/L.

Cumulative sulfate release to the water covers overlying the four barrier layers of 3 and 10-cm ranged from 38 mg to 46 mg sulfate (Figure 25). This was roughly half the cumulative sulfate release (83 mg) observed for the 1-cm depth barrier layer. As with the other test columns, correcting the sulfate mass release to the pore water for the mass attributed to residual sulfide oxidation products, resulted in negligible sulfate release to the pore waters. During the period of time assumed to represent sulfide mineral oxidation beneath a subaqueous layer of taconite tailing mixed with compost, sulfate release rates were observed to decrease as the depth of taconite tailing layer increased (Figure 26). Observed sulfate release rates to the water covers were 0.41, 0.17, and 0.07 mg/week for the 1, 3 and 10-cm depth barrier layers, respectively (Table 12, section 4.5.2). The amount of compost (0.1% - 1%) did not affect sulfate release rates.

Figure 23. The addition of compost to the tailing barrier layer resulted in a small increase in water cover pH to the 7.5 – 8.0 range. Sulfate concentrations were generally less than 10 mg/L with the exception of the 1-cm/0.1% compost barrier layer which reached 26 mg/L by week 298.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

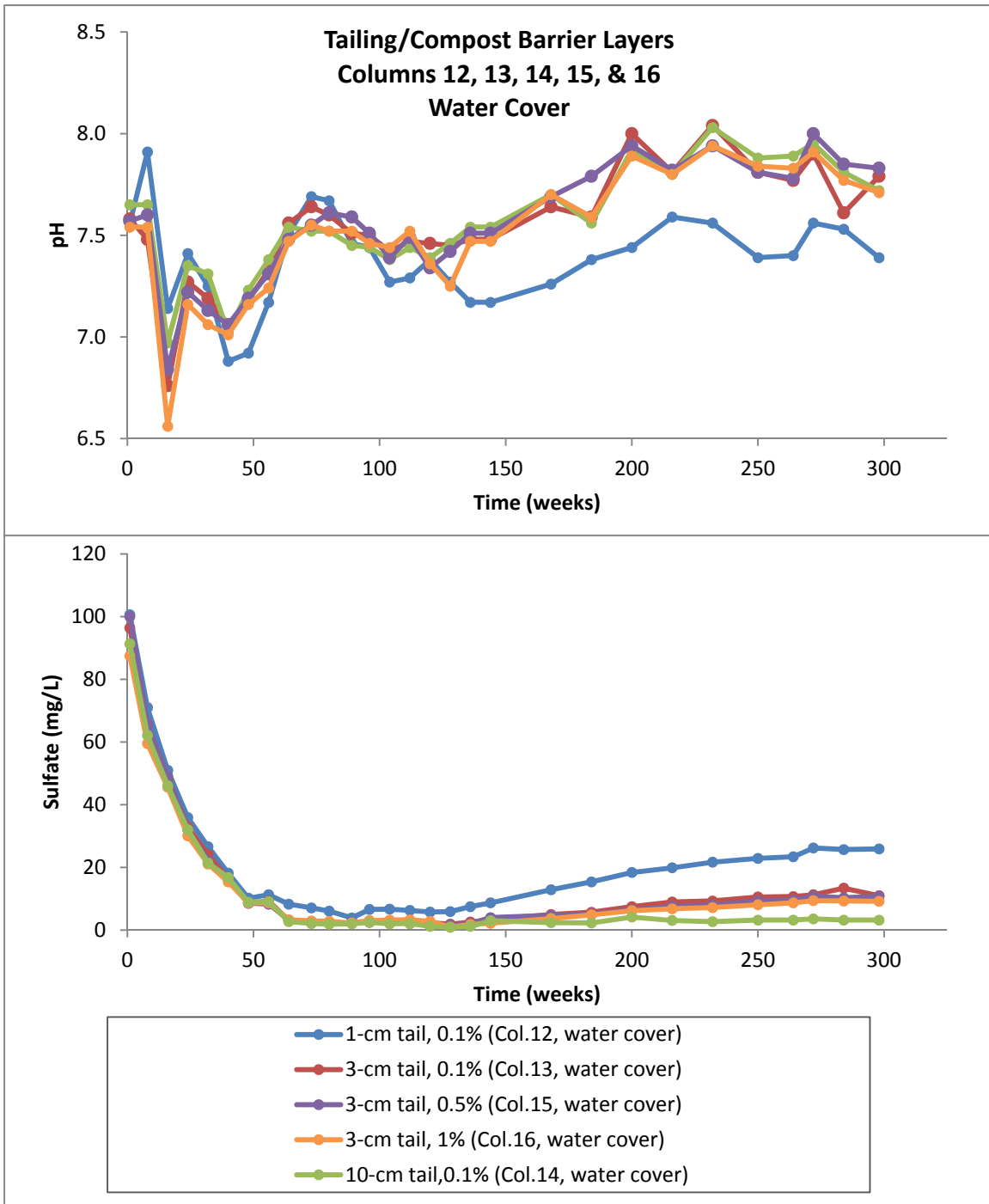


Figure 24. The addition of compost to the tailing barrier layer resulted in a small increase in pore water pH to the 7.5 – 8.0 range. Sulfate concentrations were generally less than 10 mg/L during the desired rate period of 157 to 306 weeks.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

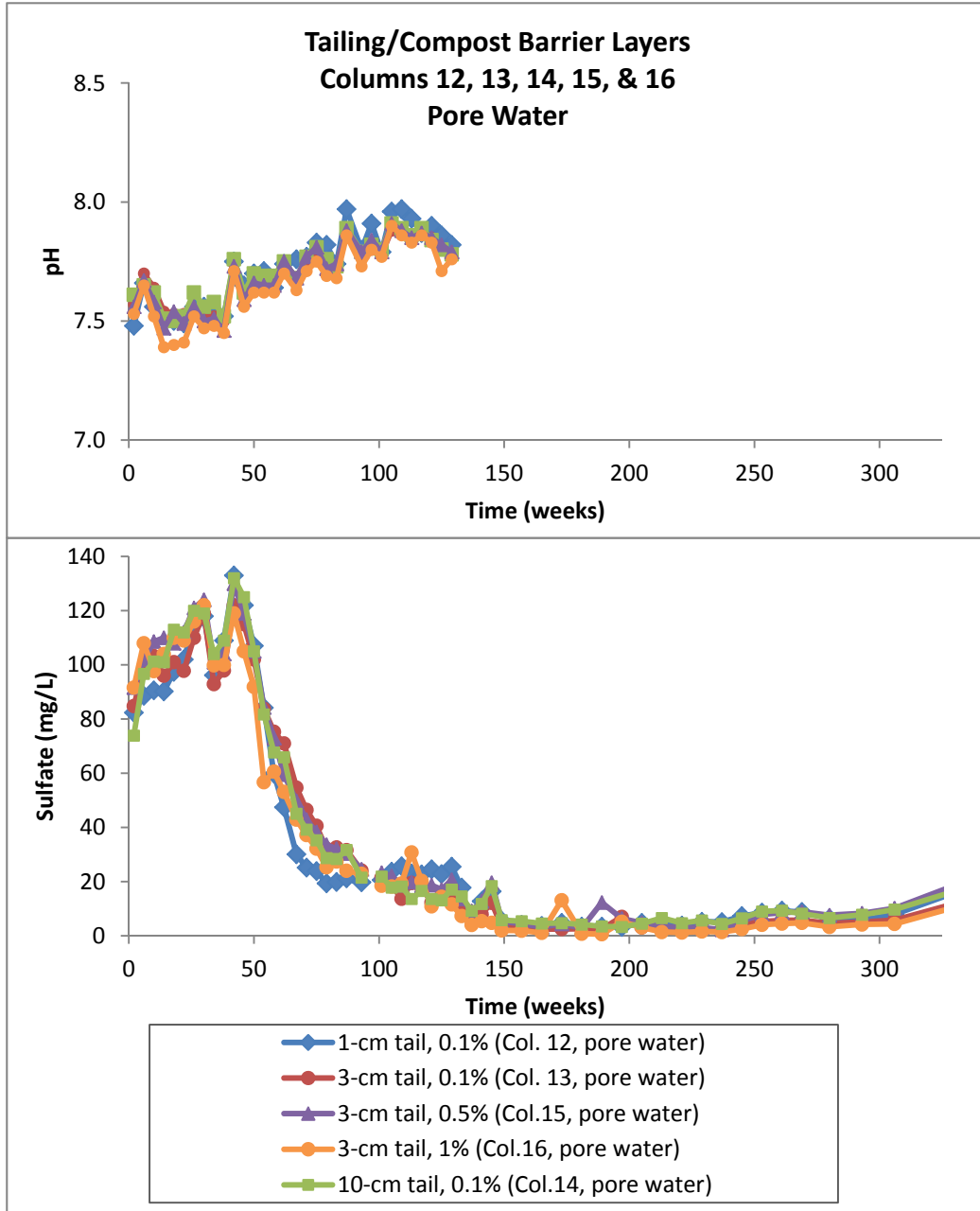


Figure 25. Cumulative sulfate release from subaqueous Duluth Complex waste rock beneath a layer of taconite tailing mixed with composted yard waste. Sulfate mass release to the water cover for the 3 and 10-cm thick layers were approximately 40 mg, roughly half the observed value for the 1-cm thick layer. Sulfate mass release to the waste rock pore waters was fairly constant, indicating steady state conditions.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

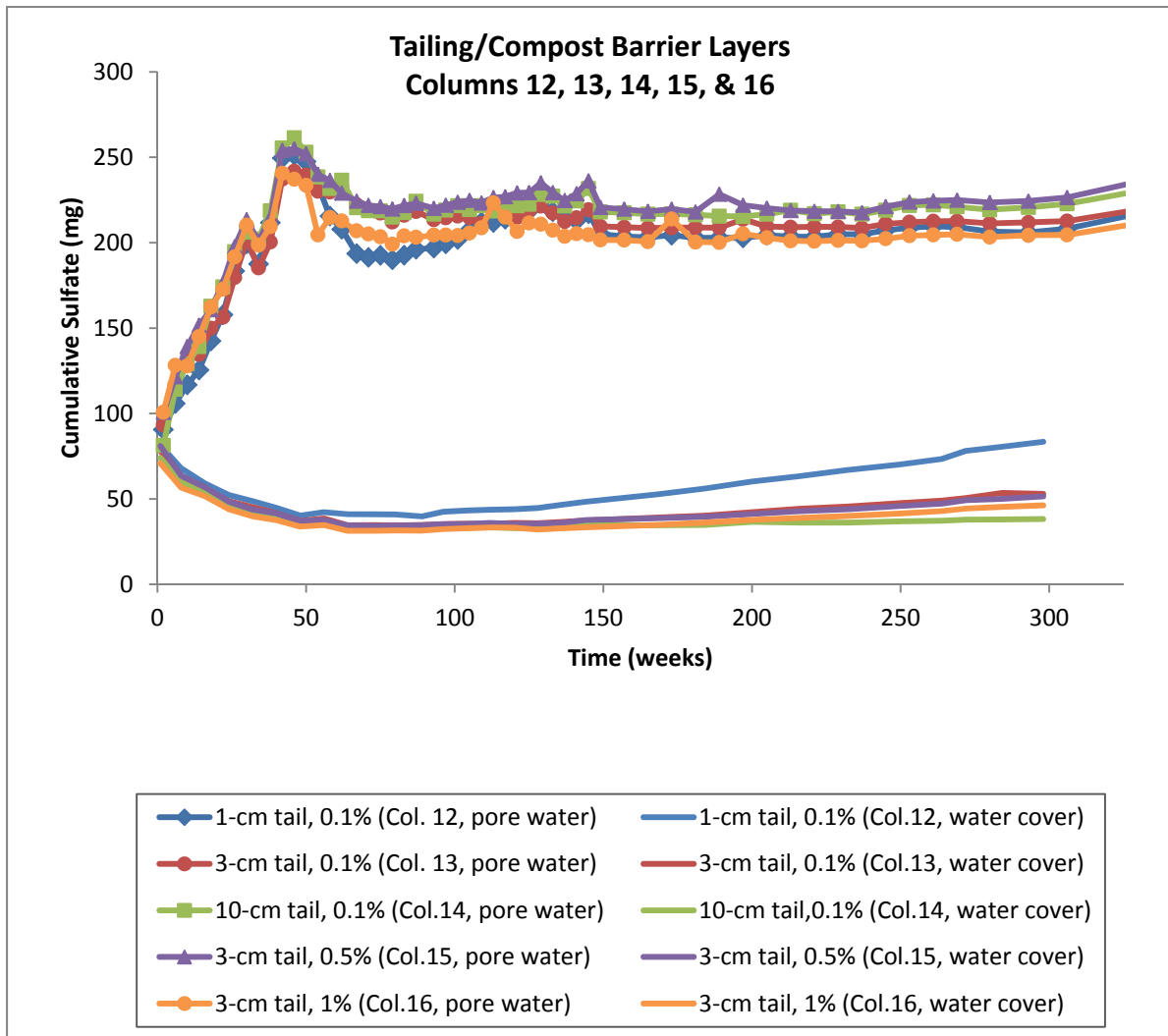


Figure 26. Sulfate release rates from subaqueous test columns 12 - 16 decreased as the depth of the taconite tailing barrier mixed with composted yard waste increased. These rates appeared to be independent of the amount of compost used (0.1% - 1%) with a 3-cm thick layer.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**

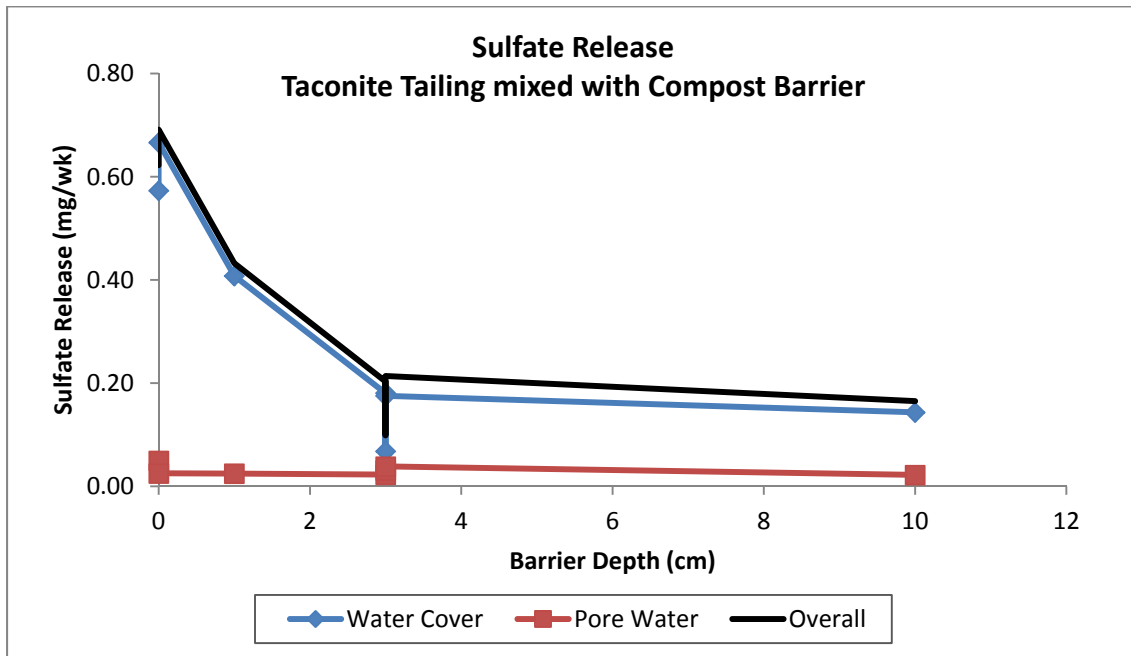


Table 12. Sulfate release rates to the water cover decreased as the depth of the taconite tailing barrier layer increased. The addition of 0.1-1 % oxygen-consuming composted yard waste to the taconite tailing barrier layer did provide any additional benefit.

		<b>Sulfate Release Rate [mg/week]</b>				
	Rate Period (weeks)	Column 12 1-cm tailing 0.1% compost	Column 13 3-cm tailing 0.1% compost	Column 15 3-cm tailing 0.5% compost	Column 16 3-cm tailing 1% compost	Column 14 10-cm tail. 0.1% compost
<b>Water Cover</b>	<b>144-298</b>	<b>0.41</b>	<b>0.18</b>	<b>0.18</b>	<b>0.14</b>	<b>0.068</b>
Pore Water	157-306	0.025	0.023	0.038	0.022	0.031
Overall		0.43	0.20	0.21	0.16	0.10

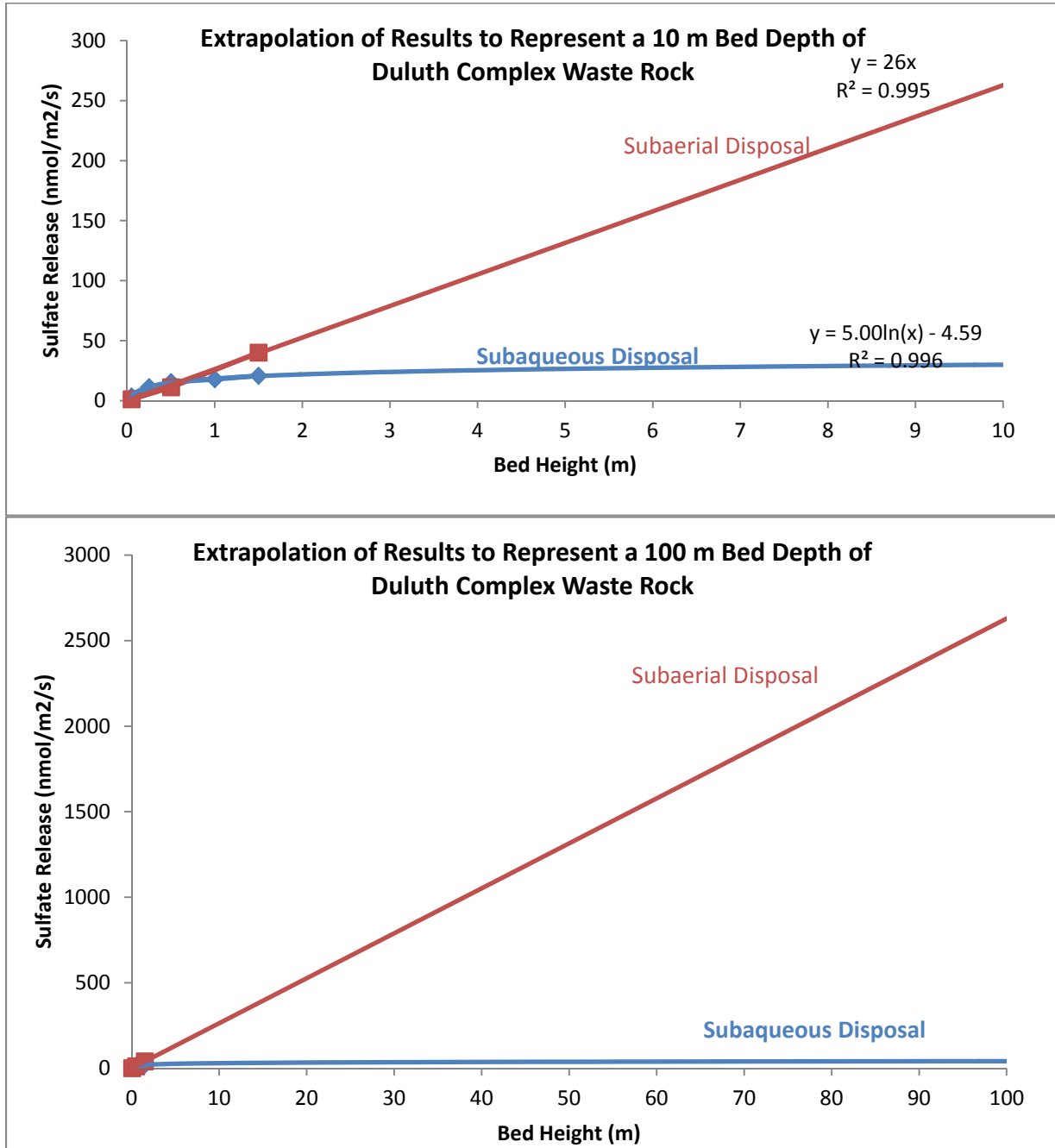
## 6. Discussion

### 6.1. Waste Rock Bed Depth Considerations for Subaqueous Disposal

The overall objective of these experiments was to investigate the effectiveness of subaqueous disposal of sulfidic mine wastes. While the mass of rock used in these column experiments was not large, these results can be extrapolated to provide insight into potential benefits of subaqueous disposal in the field. The preliminary Bed Depth Study column experiments using the coarse grained (-3/4 in. - + 1/4 in.) Duluth Complex waste rock demonstrated that subaqueous conditions reduced the rate of sulfide mineral oxidation to half that observed under subaerial conditions (Table 7, Figure 7). The relationship between sulfate release rates (per cross sectional area) and the waste rock bed depth in the subaerial simulations was linear. Thus, the rate of sulfate release from sulfidic waste rock in a subaerial setting increased as the rock bed depth, and therefore mass of sulfide mineral, increased. This trend was not observed for the same rock in a subaqueous environment, where sulfate release rates (per cross sectional area) plateaued after a bed depth of approximately 50-cm. This relatively constant sulfate release rate from the thicker rock beds implied that the waste rock itself acted as a barrier to oxygen diffusion. Rock in this upper layer essentially consumed all oxygen diffusing downward leaving the underlying rock anoxic and, therefore, incapable of oxidation. It further implied that a large mass of sulfidic waste could be disposed of in a thick bed under subaqueous conditions without significant increase in sulfide mineral oxidation.

By extrapolating these results to represent a deeper bed depth, the additional benefit of subaqueous disposal of a large mass of sulfidic waste rock, for example a mined out pit, can be examined. Sulfate release rates for subaerial and subaqueous settings in these column experiments were similar for rock bed depths less than 100-cm. However, extrapolation of these results to a waste rock bed depth of 10-m suggests that sulfide oxidation rates from waste rock in a subaqueous environment less than three percent of those in a subaerial setting (Figure 27). As the depth of rock increases, sulfate release rates in the subaqueous setting remains constant while those for subaerial disposal increase linearly with depth. These estimates represent a conceptual, semi-quantitative description of how sulfide oxidation rates in Duluth Complex waste rock vary with increasing bed depth. It is important to note, however, that the greatest benefit of subaqueous disposal would presumably be lost if a large mass of sulfidic waste was disposed of in a relatively thin (e.g. less than 100-cm) layer of waste rock.

Figure 27. Sulfate release rates, and therefore sulfide mineral oxidation, from the Preliminary Bed Depth Column Study extrapolated to represent a relatively thick bed of waste rock demonstrates the potentially enhanced benefits of subaqueous disposal compared to subaerial disposal. The displayed trendlines are merely best fit and represent a semi-quantitative description of how rates might vary with increasing waste rock depth



## 6.2. Effectiveness of Subaqueous Tailing Barrier Layers

The objective of the second phase of column experiments was to evaluate the effect of placing various barrier layers above sulfidic mine wastes disposed in a subaqueous setting. The intent of these barriers was to further inhibit oxygen transport to the mine waste, and therefore, decrease the rate of sulfide mineral oxidation. Each of the fourteen barrier layers tested inhibited sulfide mineral oxidation relative to the subaqueous controls (Figure 28). Examination of sulfate release rates from each of the barrier layer columns at any specified depth indicated that the neither limestone nor compost amendments to the taconite tailing layers affected sulfide mineral oxidation rates (Figure 28). While the pH of the water covers above the limestone-amended barriers was somewhat elevated (8.0 vs 7.5, compare Figures 8, 15, 19 and 23), the presence of limestone did significantly impact sulfide oxidation rates. Also, the relatively small amount of organic matter in the form of composted yard waste did not appear to consume enough dissolved oxygen to reduce sulfide mineral oxidation any more than the taconite tailing alone.

The consistency in these results indicated that sulfide mineral oxidation rates depended on the depth of the taconite tailing barrier layer used rather than the specific material used in the barrier layer. Plotting oxidation rates normalized to the cross sectional area of the column against the barrier layer depth rather than material shows this trend (Figure 29). A 3-cm barrier layer reduced sulfide oxidation to 25 - 50% of that observed in the subaqueous controls (0-cm depth). The 5-10 cm barrier layers reduced sulfide oxidation to roughly 20% of the subaqueous controls. These results were consistent with what would be expected in a transport-limited system, where the rate of sulfide mineral oxidation was dependent on the rate at which oxygen could diffuse through a barrier layer to reactive mineral surfaces. It is important to note, however, that this experiment was limited to specific taconite tailing barriers. These results should not be generalized to taconite tailing amended with larger amounts of limestone, organic matter or, alternatively, different types of materials.



Figure 28. Sulfate release to the water cover (normalized to the cross sectional area of the waste rock) was independent of the type of material used in the taconite tailing barrier layer. (rock bed depth = 120-cm; water depth = 40-cm)

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S, 120-cm)**

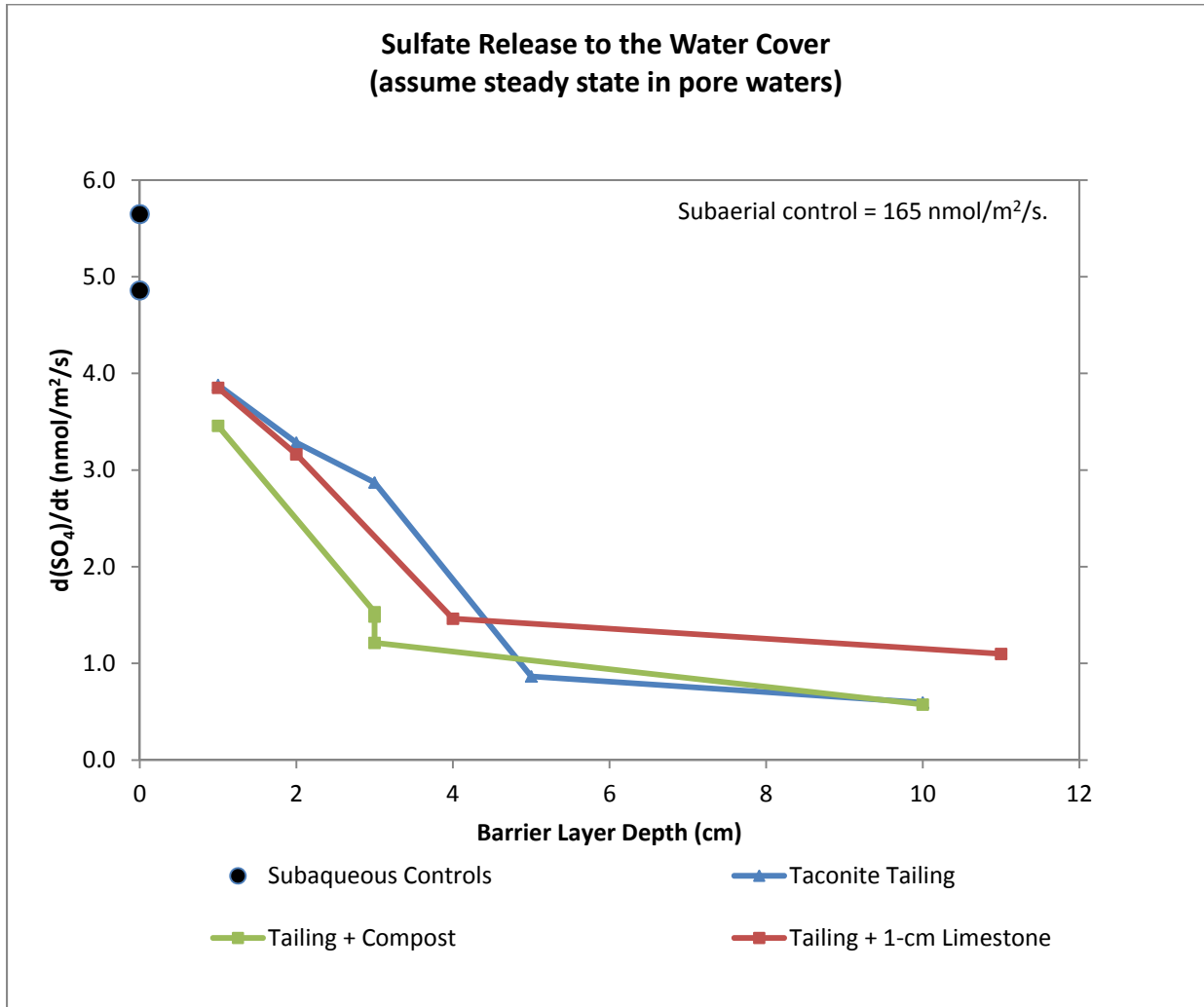
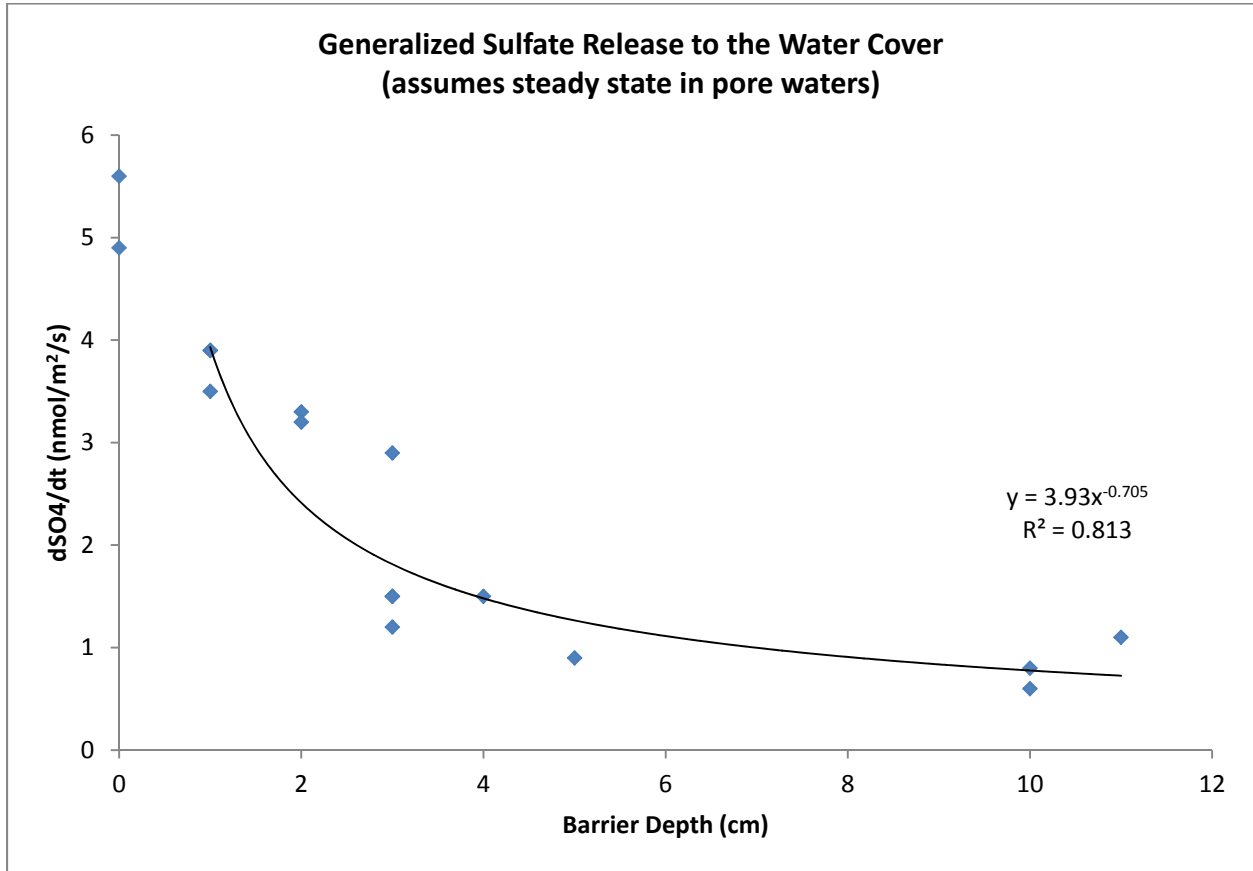


Figure 29. Sulfide mineral oxidation rates normalized to cross-sectional area were primarily dependent on the depth of the taconite tailing barrier layer. Generalizing the barrier layers for a specified depth (blue diamonds), rather than by material used, produced similar oxidation rates for that depth. The black line represents a power trendline for these data and was chosen to represent a “best fit” rather than indicate specific quantification



### 6.3. Observed Acid Production Rates and Oxygen Diffusion Control

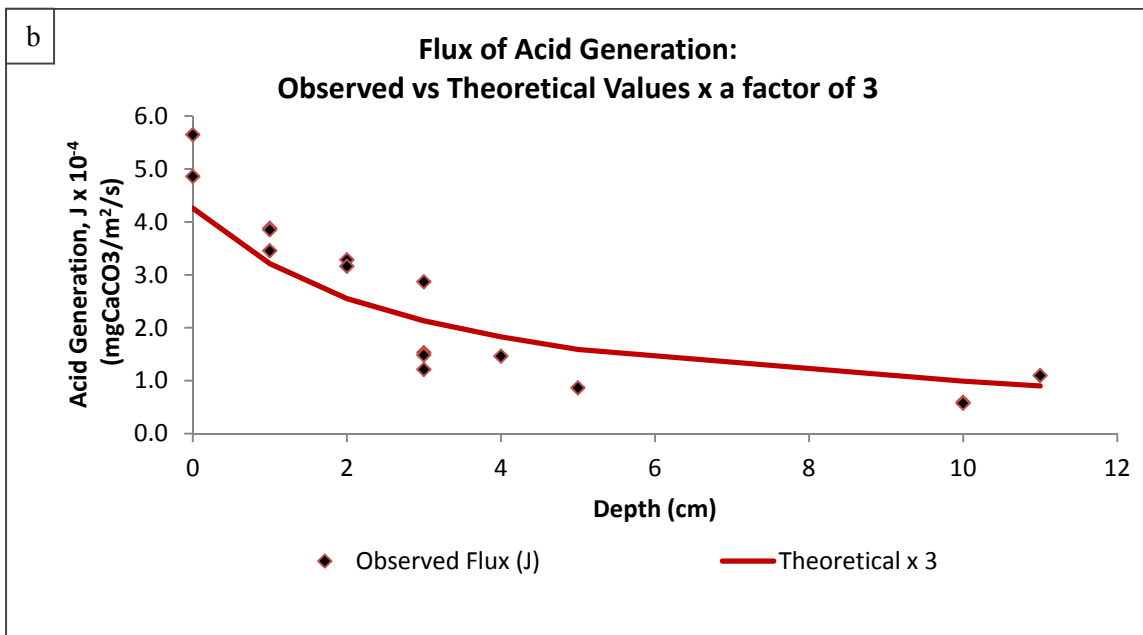
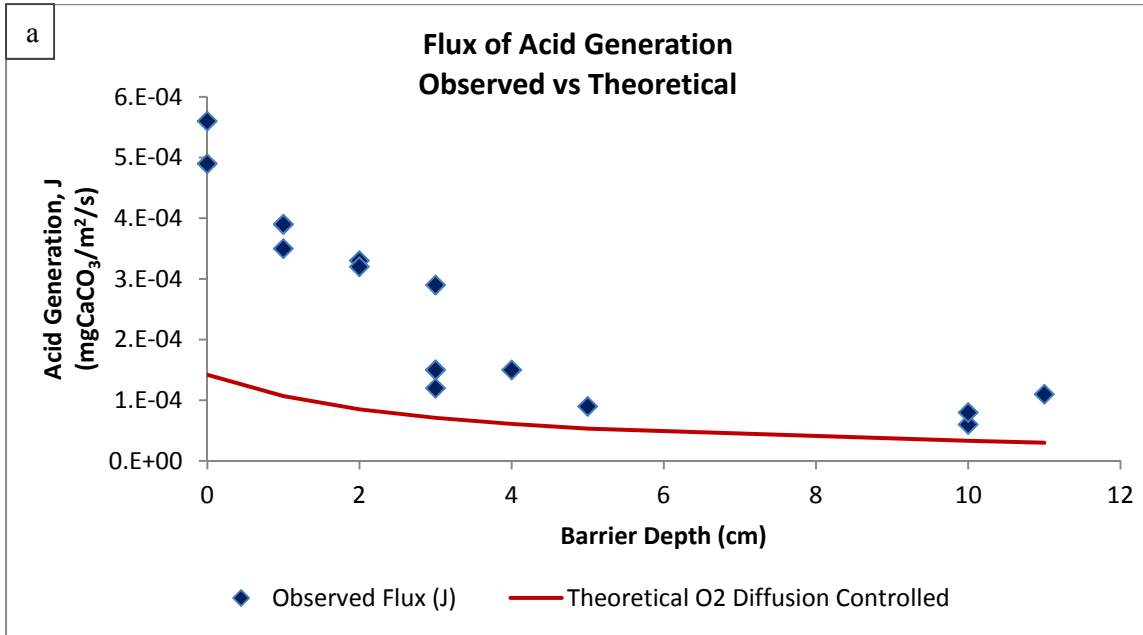
Rates of acid generation when oxygen transport is limiting can be calculated using the approach by Morin (1993). This approach assumes the water overlying the mine waste is saturated with dissolved oxygen and the water within the mine waste is stagnant. Since pore water samples were obtained from the bottom of the columns, oxygenated water was drawn down through the tailing bed. Thus, the second assumption is not particularly valid in these experiments, and sampling procedures must be considered when comparing acid production rates from these experiments to theoretical calculations.

Based on calculations of theoretical oxygen diffusion through an inert layer, observed acid generation was greater than expected (Figure 30). Advective transport of oxygen due to sampling may, in part, be the cause of these elevated rates. However, the difference between theoretical rates and those observed in the subaqueous controls and shallow (1-2cm) barrier layer columns was too large to be explained by advective oxygen transport alone. At the time of this report, no quantifiable explanation for these results has been determined.

Observed acid production for the deeper (3-11 cm) barrier layers was in closer agreement to the expected theoretical values. Taking the presumed contribution due to advective oxygen into account, the observed acid generation from waste rock beneath 3 – 11 cm deep barrier layers (excluding the 3-cm taconite tailing layer) were in fair agreement with the theoretical rates (Figure 30a). Although the theoretically determined values don't agree with the data, it was found that they were consistently off by a factor of roughly 3 (Figure 30b). The reason for this discrepancy has yet to be identified. Sensitivity analysis indicated that the calculation was not greatly affected by the reaction rate value used. However, the fact that the theoretical unifying equation fits the shape of the data, despite the discrepancy, suggests that the rate of sulfide mineral oxidation may be oxygen diffusion-controlled for waste rock stored in a subaqueous environment beneath a 3-11 cm barrier layer of taconite tailing.

Figure 30. Observed sulfide oxidation rates were elevated by a factor of approximately 3 when compared to theoretical diffusion-controlled calculated values (red line). However the shape of the theoretical curve matched the data well, indicating that sulfide mineral oxidation rates were likely controlled by diffusion of oxygen to reactive mineral surfaces at depth.

**Barrier Layer Columns: Duluth Complex rock  
(Arimetco -  $1.40 \leq d \leq 4.75$  mm, 0.85% S)**



## 7. Conclusions

Previous batch experiments indicated that although abiotic sulfide mineral (i.e. pyrrhotite) oxidation did occur, subaqueous oxidation rates were not accelerated due to biological mediation as observed in on land (subaerial) disposal scenarios. The batch experiments focused on oxidation at the rock-water interface. The laboratory column studies described herein investigated subaqueous sulfide oxidation rates of a deeper rock bed. These experiments also evaluated the effectiveness of using taconite tailing, taconite tailing with an additional layer of limestone and taconite tailing mixed with composted yard waste as a barrier to oxygen diffusion to pyrrhotite-bearing mine wastes in a subaqueous environment.

Preliminary column experiments (Subaqueous Bed Depth Column Study) were used to determine the minimum bed depth required for oxygen diffusion to limit sulfate release rates in a subaqueous environment. Five columns of fine-grained ( $0.053 < d < 0.149$  mm) tailing and five columns of coarse grained ( $6.53 < d < 19.05$  mm) waste rock using bed depths ranging from 1 to 150-cm. Over the 83-week period of record, the pH of the water from the ten subaqueous columns typically fluctuated between 6.5 and 7.5. Sulfate concentrations were generally constant throughout the period of record, with averages typically in the range of 6.0 to 11.0 mg/L for the fine grained tailing and 1.4 to 7.7 mg/L for the coarse waste rock. Minimum bed depth requirements for fine and coarse fractions were determined to be 20-cm and 100-cm, respectively. The results were also used to conceptually exemplify the benefit of subaqueous disposal over subaerial disposal as a function of waste rock depth.

The second phase of column experiments examined the effectiveness of various taconite tailing barrier layers above Duluth Complex waste rock at inhibiting oxygen diffusion, and therefore, sulfide mineral oxidation (Barrier Layer Column Study). The barriers under examination were taconite tailing (1, 2, 3, 5 and 10-cm), taconite tailing with an overlying layer of limestone (0, 1, 3, 10-cm tailing and 1-cm limestone), and taconite tailings/yard waste compost mixtures (1, 3 and 10-cm tailing with compost mixtures of 0.1 – 1%).

Roughly three pore volumes of flow were required to remove reaction products released due to oxidation of the rock used prior to the inception of the experiment. This provides a basis for estimating removal of similar residual solute under operational conditions. All the barrier layer materials examined produced similar water chemistry. Surface and pore water pH from each of the barrier layer test columns and the two subaqueous controls remained above 6.0 throughout the 300 week period of record. In contrast, the drainage pH of the subaerial control column decreased below 6.0 within 134 weeks. As with the pH, sulfate concentration trends in the water covers and pore waters within these columns were generally independent of the barrier layer materials.

Sulfate release rates ranged from 0.1 – 0.5 mg/week for the barrier layer columns as compared to approximately 0.6 mg/week in the subaqueous control columns. These results indicated that the barrier layers did inhibit oxygen diffusion to the mine waste, and that barrier layer depth was the primary rate controlling factor. A taconite tailing barrier of 5-cm was effective at reducing sulfide oxidation to 20% of that observed in the subaqueous control columns. Additional

incremental reduction was observed as barrier depth increased to 10 cm. Addition of a limestone layer above the tailing or composted yard waste mixed into the tailing did not provide any further reduction in oxidation rates.

Comparison of the observed acid production rates from the columns to theoretical values calculated based on oxygen diffusion alone, indicated that the rate of acid production from waste beneath a 5-cm tailing barrier layer was probably diffusion-controlled. However, advective oxygen input due to sampling likely elevated acid production rates. A theoretical diffusion equation fit the shape of the data but, quantitatively, was roughly one third the observed values. Despite the quantitative discrepancy, it is concluded that 3-11 cm barrier layers of taconite tailing inhibit oxidation of underlying sulfide minerals by limiting oxygen diffusion rates.

Although both subaqueous disposal and the implementation of barrier layers above rock disposed in a subaqueous setting inhibit sulfide mineral oxidation, certain precautions are clear. The rates of acid generation for subaqueous conditions and residual acidic salts accumulated on mine waste surfaces must be considered to ensure that acid conditions would not develop in a mine upon subaqueous disposal of sulfidic mine wastes. Sources of potential neutralization, such as alkaline water inputs to the mine, dissolution of alkaline components in the mine walls and the use of alkaline amendments must be quantified. Furthermore, the potential impact of slow release of trace metals from sulfide minerals into neutral waters must be assessed.

## 8. Acknowledgments

Funding for this report and laboratory work since July 2011 was provided by Minerals Cooperative Environmental Research and Iron Ore Cooperative Research state funding plus industry match. Funding for laboratory work prior to July 2011 was provided by State general fund. Solid-phase chemical and mineralogical analyses were conducted by Don Schnortz of Lerch Brothers (Hibbing, MN) and Louis Mattson of Midland Research (Nashwauk, MN), respectively. The dissolution experiments were conducted by Pat Geiselman and John Folman under the direction of David Antonson. Anne Jagunich and Sue Saban were responsible for data management.

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